Industrial and Engineering Chemistry

Vol. 18, No. 2 FEBRUARY 1, 1926

Congressional Inquisition

HOUSE RESOLUTION 75 was introduced in the 69th Congress on January 6 by Mr. Frear of Wisconsin, was referred to the Committee on Rules, and ordered to be printed. The purpose stated is "to investigate the means and methods of control and production of chemicals and dyestuffs and for other purposes." Its full text follows:

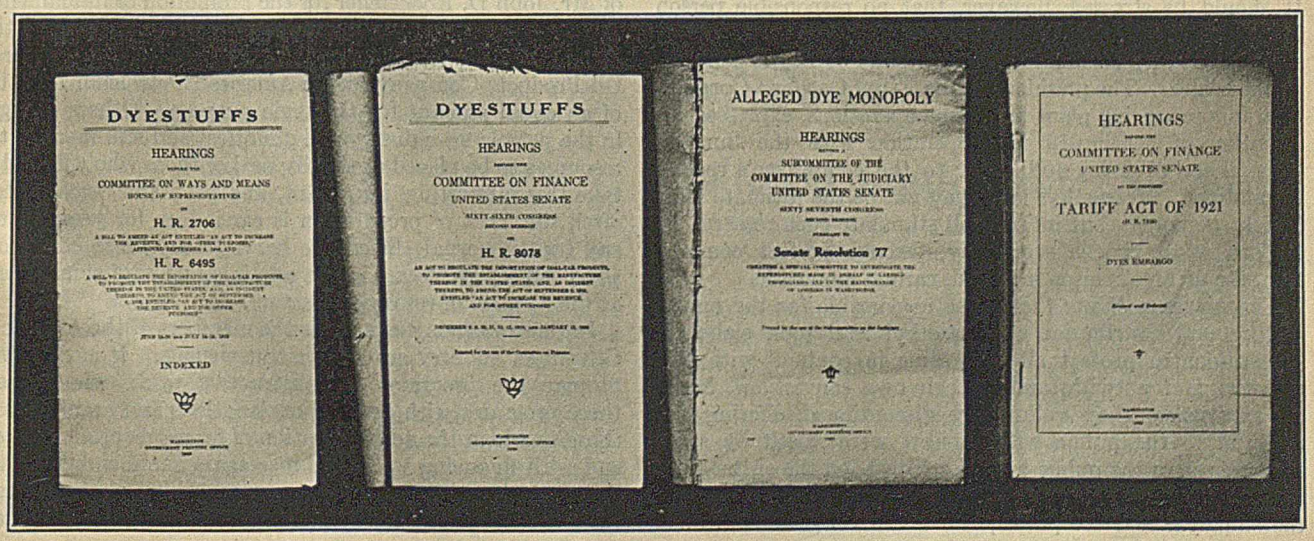
Resolved, that the Committee on Flood Control be, and it is hereby, authorized and empowered to investigate the means and methods of the control of production in the United States of chemicals and dyestuffs, together with prices, secret agreements, if any, and profits and whether the tariff rates in force effect a practical embargo against dyestuff imports so as to maintain a monopoly. Said committee shall have leave to report by bill or otherwise at any time on the matters therein stated.

We assume that the reason no other committee was given an opportunity to conduct this investigation is that Mr. Frear has a place on the Committee on Flood Control, and if the House finally adopts the resolution he will be there to see to it that everything is done to carry out whatever he had in mind.

Investigations, hearings, reports—more investigations, more hearings, and more reports! We have lost count of the investigations, hearings, and reports sponsored by Congress in the last few years, but it is hard to reconcile the policy of economy with this uncontrolled appetite of Congress for investigations. We illustrate here four printed reports of hearings bearing upon chemicals, dyestuffs, and the like. The first runs into 735 pages; the second, 624; the third, 1477; and the fourth, 775. At least one thousand copies of each hearing are printed and every member of Congress receives one. There is no way of estimating just what these hearings have cost. Their mere reporting and printing represents a very considerable sum, not to mention the time of the committee, perhaps the least important item, and the time of the manufacturers away from duties of business administration, which is by all odds the most important. The worst of it is that nothing seems to happen.

The "Alleged Dye Monopoly," a hearing occupying nearly 1500 printed pages, was printed in 1922. It grew out of certain charges made by Senator King, who was under the impression "that the dye industry is controlled by a combination of corporations and that it is in fact a monopoly, and that in order to maintain such a monopoly and obtain an embargo against the importation of competing dyes, it has employed agents, attorneys, and lobbyists to influence Congress in behalf of special legislation in the interest of such dye monopoly." The matter was gone into exhaustively, the hearing beginning on February 20, 1922, and continuing through May 16, 1922, with a subsequent hearing on June 3, 1922. But to this day the committee has made no report. Members of the committee have informally stated that the evidence showed no monopoly to exist, but there has been no formal report. We wonder why?

In addition to the books illustrated below, Mr. Frear and his committee have at their disposal much information and other documents, notably the records of the Chemical Foundation suit, prices that have been collected and published by the Tariff Commission, and many facts that could be reported by the Bureau of the Census, and so the man who believes in efficiency and economy wonders what it is all about, what the real purpose is, and just how representative of the average American these representatives in Congress are. We have had enough of investigations and reports. Let those who are dissatisfied familiarize themselves with the data already accumulated before they seek to impose upon the country the burden of additional investigations, further hearings, and more printed reports.



Ethyl Gasoline Again Available

IT WILL be recalled that in May, 1925, Surgeon General Hugh S. Cumming of the Public Health Service invited those interested in the problem to meet in a conference under his chairmanship and discuss such data and theories as might be presented relative to the alleged hazard in the manufacture, distribution, and use of tetraethyl lead as an antiknock compound in gasoline. The committee appointed was asked to consider the hazards involved in the retail distribution and general use of tetraethyl lead and was expected to report as near January 1, 1926, as possible. The committee has now made its report, which we are glad to print on page 193 of this issue. Later, there will be available through the Public Health Service copies of the data, methods, and all other records upon which this brief report is based.

It was fortunate that so distinguished a group of men as those composing the committee, under the chairmanship of William H. Howell, professor of physiology at the Johns Hopkins School of Hygiene and Public Health, could supervise the investigation and could serve without remuneration, there being no appropriation from which even a modest honorarium could be paid. They have rendered valuable service to the public, and as the result of this report it is hoped that means will be provided whereby other groups of scientists may undertake other investigations of possible hazards well in advance of any emergency.

The report, which was presented by the chairman of the committee before an open conference on January 19, confirms the excellent piece of work done some time ago by the Bureau of Mines under the direction of Dr. R. R. Sayre and also the results reported by Dr. R. A. Kehoe of the University of Cincinnati. The results of these investigations had previously been severely criticized and it is, therefore, a pleasure to record the confirmation of their work by the present committee. It is expected that even before this comment can appear regulations will have been formulated as suggested by the committee. In conference with state health officers, representatives of the manufacturers, the distributors of tetraethyl lead gasoline, and representatives of labor reasonable regulations will be drafted. It will then remain for the individual municipalities and states to take such action as seems best to them to make again available to the gasoline-using public this chemical mixture which offers such great economies.

With the resumption of the distribution of ethyl gasoline many new developments may be anticipated. The redesign of automobile motors may be expected. The use of new materials will be encouraged and many economies effected. It should be stressed, however, that no responsible person identified with any phase of the automotive industry desires to see any economic progress made at the expense of public health. The president of the Ethyl Gasoline Corporation, in announcing plans to resume operations, expressed his intention of continuing in coöperation with the Surgeon General and of giving full effect to the committee's recommendations. Tetraethyl lead may not be the ultimate antiknock compound, but its use will stimulate such research on motors as to abolish eventually, through perfect combustion, the greatest poison involved, carbon monoxide.

The evidence shows that those responsible for the manufacture and distribution of tetraethyl lead took elaborate precautions to protect all who came in contact with the material and notwithstanding their own convictions, based on experience, they voluntarily discontinued offering the material to the public when doubts were raised by some scientists as to the public hazard. Too often the enthusiasm of the manufacturer leads him to minimize hazards both to the employee and the public, and his investigations are not so thorough as could be wished. Then, too, in contrast with the present case, often an emergency may arise and pressure be brought to bear upon him before he discontinues manufacture. There are many other hazards in industry to the workers engaged in production, as well as to the consuming public, which merit equally careful investigation and experiment. Certain substitutes for ethyl alcohol in the preparation of food products are being offered and used without sufficient scientific data as to their influence on public health. The investigation serves to emphasize the necessity of requiring adequate ventilation and cleanliness in garages and automobile repair shops. Hazards in no way related to ethyl gasoline are known to exist in the majority of such places. No time should be lost in enacting municipal ordinances and state regulations to guarantee safe conditions.

The ethyl gasoline investigation was carried on with public health funds available only at considerable sacrifice to other investigations. If the ethyl gasoline study is to be continued as it should be and if, under its ample authority, the Public Health Service is to conduct investigations along other lines affecting hazards in industry and public health, adequate provision must be made in the budget. The scope of its work is not limited by authority. It is limited wholly by a lack of personnel and facilities, which is another way of saying appropriations.

At the conclusion of the conference a motion was adopted recommending that Congress be asked to provide money to carry on such important work, and it is hoped that there will be no lack of support whenever the officials of the Public Health Service request sums with which to conduct the scientific work really necessary to protect the public.

In the ethyl gasoline investigation chemistry, in the hands of those trained in the methods, supplied many of the data which will save for general use a compound introduced by another group of chemists. Chemistry can save industries if called upon in time. It may even resurrect an industry, but it is far better to seek its aid when the industry shows the first signs of indisposition.

Working Leaven

IN GALATIANS we read that "A little leaven leaveneth the whole lump," and while no mention is made of the influence of temperature and concentration on the rate of leavening, we have many practical examples to show their influence.

In January it was our privilege to comment upon the gift of Mr. John D. Rockefeller for the promotion of fundamental research in the petroleum industry. On page 189 of this issue it is our pleasure to announce the gift of the Universal Oil Products Company to the American Petroleum Institute of an equal amount for the same purpose. Others engaged in the petroleum industry will doubtless add still more to the resources to be placed at the disposal of those who will undertake this interesting, important, and profitable work. How often the work of preparation is carried on for years before any fruit is borne! Then the harvest may be so bounteous as to call for great care in the administration of sums placed at the disposal of research directors.

In these various movements the members of the AMERICAN CHEMICAL SOCIETY are always conspicuous. It is they who prepare the programs of constructive work, who present these programs with detailed explanations and arguments to those to whom the administration of large resources is given, and with financing well done it is again the members of the SOCIETY who more often than not are called upon to direct the work, to do the work, and to obtain the results. There

are many pieces of constructive work that may some day be directed by the AMERICAN CHEMICAL SOCIETY with funds entrusted to it. Soon it will be demonstrated to those who constantly stand ready to invest a part of their wealth in worthwhile going projects that the AMERICAN CHEMICAL SOCIETY is an organization alive to the needs of the age and possessed of the ability to get the most out of any possible expenditure. Let the good work continue!

Civil Service Appointments

WE CAN all agree that, regardless of the place to be filled, the best progress will be made when the best man obtainable is selected for the work. We have held that one handicap in the administration of a government bureau and, for that matter, some university departments as well, lies in the fact that the director is denied the power of so organizing the bureau as to obtain maximum results. He is given responsibility without the authority to hire and fire, and what he can accomplish is all too frequently limited by the character of his personnel inheritance. We can also agree that the one reason why the procedure followed in successful business cannot be followed in government employment is due to our political system wherein those in power seek to maintain their position by obtaining the appointment of those who have assisted or will assist them. In the past if a bureau director, unprotected by Civil Service, were to decline to appoint the candidate of an influential Congressman, he would invite disaster through sharp decreases or perhaps entire absence of appropriations.

And so the Civil Service Commission was set up to take out of politics the appointment of certain classes of government employees. In the past this has not accomplished all that was hoped. Ways were discovered for getting around the Civil Service provisions. In days gone by specifications for a particular position have been so drawn as to eliminate all but two or three candidates. In some cases where the bureau chief stated there was no one on the eligible list who exactly fitted a particular requirement, he was permitted to make a temporary appointment pending certification by the Civil Service Commission. In due course an examination was announced and those not familiar with the fine points of the system thought that by taking the examination they had a chance at appointment. But, alas, they were doomed to disappointment! The examination had been prepared with reference to the temporary appointee and the director could choose any one of the three making the highest marks. Notwithstanding the efforts of the Civil Service Commission, there have been announcements indicating positions open when, as a matter of fact, those familiar with the system knew that in reality such was not the case.

In spite of these abuses, the Civil Service has done a great deal to obtain competent, high-grade men and women for government positions and to protect them while engaged in their work. Now a new era has come and we heartily approve of the latest procedure, which will be adopted to govern future appointments.

When a vacancy occurs among the higher grades, the bureau chief will hereafter be expected *at once* to make known to the Civil Service Commission whether that vacancy is to be filled, what the specifications are, and to inquire whether there are any eligibles that can be certified by the Commission as available for appointment. If there are, the Commission will certify three names for the director to make a choice. If the director finds none of those certified satisfactory, he must state in writing why he cannot recommend appointment, and if these reasons satisfy the Commission it will proceed to a new examination. The important point comes not only in this procedure but in the method of grading the examination papers. Where important posts are to be filled, the papers will be graded by a committee, the chairman of which will be a representative of the Civil Service Commission, and the members three disinterested qualified persons in addition to a representative of the bureau concerned. The persons composing the committee will be, for the purpose of grading these papers, examiners of the Civil Service Commission. Additional safeguards are the care exercised by representatives of the Commission to see to it that in no case are specifications written to make the path of one man easy and the refusal to sanction appointments pending certification in cases where there has been any delay in requesting some one to fill a vacancy.

We believe these new procedures and policies will go a long way toward preventing a repetition of past abuses and wish to do whatever we can to assist the Civil Service Commission in securing for government service the best qualified men available.

Industry's Tribute to Research

PAUL SABATIER, who has made such important contributions to the science and technology of catalysis, is to come to America in September, 1926, Procter and Gamble, of Cincinnati, having generously offered not only to make his journey possible, but, in addition, to present him with a substantial honorarium in acknowledgment of his basic research.

It was the fundamental work of Sabatier on catalysis that laid the foundation for the commercial hydrogenation of oil. Under the stimulation of American ingenuity, processes have been developed by which hard fats are now produced from liquid fats in annual quantity equal to the lard obtainable from seven million hogs. Other millions of pounds are partially hydrogenated for blending purposes, and the value of other vast quantities is increased by hydrogenation for technical purposes.

Sabatier has profited from these enormous operations only to the extent to which his world renown has been enhanced, and his place is secure in scientific history because of his fundamental research rather than the application of his results to commerce.

It has been said that industry cares little for the work of the pure scientist. But here we have an example of the voluntary tribute paid by a great industrial organization to a scientist who, for years, has worked without ostentation in his Paris laboratory. There are other scientists at home and abroad whose discovery of truths has brought large returns to those in a position to capitalize them. We trust that the example set by Procter and Gamble may not go unnoticed by all such.

Chemical Equipment Exposition

AS ANNOUNCED in the News Edition, the Association of Chemical Equipment Manufacturers has arranged an exposition to be held in Cleveland, May 10 to 15, inclusive. We are attracted by the extent to which the technical societies have offered to coöperate in this exposition. Groups representing nine national societies have formed a committee to correlate the week's technical program. We know of no similar experiment and the results will be watched with interest. Some of these societies have joined in technical programs in times past, but to bring them together in connection with such an exposition is new and should lead to better coöperation in other lines of endeavor as well.

Metallic Uranium[1,2]

Production of the Pure Fused Metal by Reduction of Uranium Chloride by Calcium in a High Vacuum

By J. F. Goggin, J. J. Cronin, H. C. Fogg, and C. James

University of New Hampshire, Durham, N. H.

THE conflicting statements concerning so many of the metals indicate that there is much need for research in this direction. An examination of the literature reveals the fact that many of these elements are extremely active, combining readily with gases and reducing most refractories with which they come in contact. It is therefore necessary, when preparing an active metal, to use pure materials, a high vacuum, a powerful reducing agent, and the most stable refractory obtainable. Great care must be used in selecting the refractory, since any reducible impurity contained therein is almost certain to contaminate the product.

Purification of Uranium Oxide

High-grade commercial uranium oxide was dissolved in nitric acid, the solution diluted, filtered, and evaporated to crystallization. The mother liquor was poured off and the crystals were dried in a centrifuge. These crystals were recrystallized and centrifuged several times. The mother liquors were submitted to fractional crystallization in order to obtain most of the uranium in the form of pure uranyl nitrate. These crystals were dissolved in water, precipitated by ammonium hydroxide, filtered, washed, and ignited.

Reduction of Uranium Oxide by Metallic Calcium

This method, which has been recommended by various writers, was tried out under varying conditions. Since uranium metal, especially in the powdered form, rapidly combines with nearly all gases, it was necessary to carry out the reduction in a high vacuum. For this purpose the apparatus

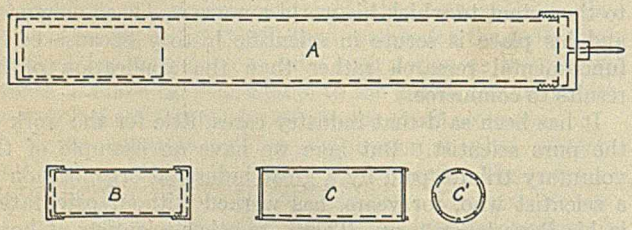


Figure 1

shown in Figure 1 was employed. *A* shows the apparatus complete with the reduction chamber in place. It consisted of a piece of large bore iron pipe (about 4 feet long) closed at one end with a welded plug. The other end was threaded and fitted with a regular pipe cap, drilled through, and tapped to take a short length of $^3/_8$-inch pipe, which was smoothly tapered to permit easy attachment of the vacuum pump.

B and *C-C'* show two types of reduction chambers. The first, used only in the preliminary work and adapted only to the reduction of the oxide, was made of a short piece (6 to 12 inches long) of iron pipe with both ends threaded and closed with pipe caps. This type was found to be unsatisfactory because the calcium vapor escaped rapidly through the caps. Form *C-C'*, which may be used in reducing either the oxide or chloride, was made of Shelby steel tubing. Tight-fitting steel plates were used to close the smoothed ends of the tube. The plates projected slightly into the inside of the tube and were fastened in place by means of eight or ten small cap screws. Chambers made in this manner were sufficiently tight to prevent the escape of any appreciable quantity of calcium vapor.

Pure uranium oxide was mixed with a little more than the theoretical amount of calcium shavings and placed in the reduction chamber. The latter was then put in the vacuum chamber and, after replacing the cap, the whole was connected with the pump and evacuated. Considerable time was allowed to elapse after the manometer ceased to show any change before heating was commenced. With the pump running, the end of the tube containing the reduction chamber was kept above a bright red heat by means of a powerful kerosene oil burner for 45 minutes, the highest temperature attained being around 1000° C. The apparatus was allowed to cool overnight, filled with dry carbon dioxide, opened, and the reduction chamber quickly transferred to a vessel containing alcohol. The contents were then slowly transferred to an ice-cold solution of ammonium chloride. After the solution had been changed several times, it was replaced by water, and the latter by alcohol. The powdered metal was next treated with alcohol containing hydrochloric acid to remove any calcium, uranium hydroxide, etc., and finally washed with pure alcohol.

The product obtained by this method consisted of a slightly brownish powder mixed with small globules very similar to that described by several previous workers. The results of an analysis showed the presence of both oxygen and iron. Since the calcium used for the reduction carried only a minute amount of iron, it was evident that the remainder came from the reduction chamber. Owing to the great activity of the finely divided metal, it was decided to search for a method which would yield a fused product at the moment of reduction. It was recognized at this stage that two vital points had to be considered: first, the necessity of a reducing agent with a great affinity for oxygen; second, that the reduced metal must be kept from coming in contact with any iron. Unfortunately, the calcium oxide produced in the reduction of a metallic oxide by calcium is infusible, and prevents the globules of metal from uniting, even if the temperature of reduction is higher than the melting point of the desired metal. Since sodium and calcium chlorides are readily fusible, it seemed that the reduction of anhydrous uranium chloride by one of these metals deserved consideration. Calcium metal appeared to be the more satisfactory of the two, since it has a very much greater affinity for oxygen, which is certain to be taken up in the form of moisture during the manipulation of the anhydrous uranium chloride.

Preparation of Anhydrous Uranium Chloride

The simplest method for the preparation of this compound is to allow chlorine and sulfur chloride to act upon the heated oxide. The essential parts of the apparatus (Figure 2) consisted of two quartz tubes, *B* and *C*, approximately 2.5 feet long by 2 inches internal diameter. These were con-

[1] Received October 19, 1925.

[2] A portion of this work was offered in partial fulfilment of the requirements for the degree of M. S. at the University of New Hampshire.

nected by a short piece of similar tubing which fitted loosely inside, the joint being made tight with a turn of asbestos paper (previously ignited) and alundum cement. The tube *C*, containing the charge of uranium oxide, usually from 800 to 1000 grams, was placed in the furnace *D*. This furnace was simply a piece of magnesia pipe covering closed at the ends by pieces of asbestos board, *a*, through which holes were cut to allow the silica tube to extend.

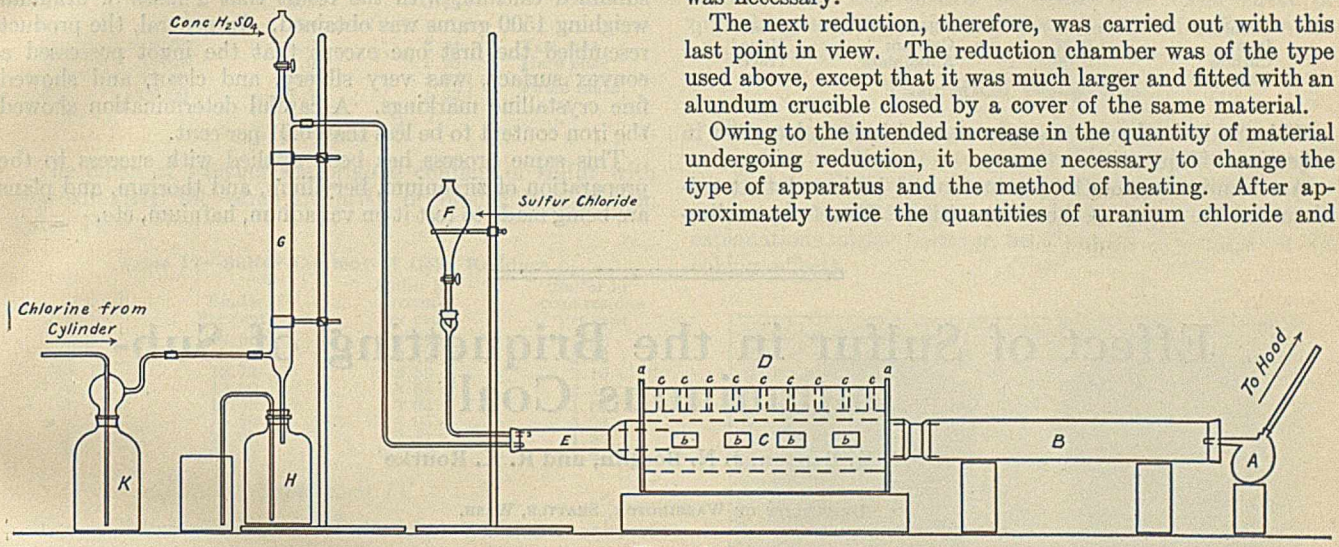


Figure 2

Heat was supplied by four powerful blast lamps, whose flames were directed through the openings, *b*, cut through the wall of the furnace. The burnt gases passed out the series of small openings, *c*, through the top of the furnace. Such a furnace allowed a high temperature to be obtained in a few minutes, and although the furnace body was good for only six or seven runs, it could be cheaply and quickly replaced. When a temperature of 900° C. or more had been reached, chlorine from the cylinder was passed through the wash bottle *K* containing concentrated sulfuric acid to indicate flow, and through a drying tower, *G*, connected to a safety trap, *H*. From the tower the chlorine passed into the quartz tube, *E*, where it mixed with the sulfur chloride coming from the dropping funnel, *F*. The tube *E* projected slightly into the high-temperature tube, *C*, where the heat caused rapid volatilization of the sulfur chloride. The uranium chloride formed in *C* was condensed in *B*. The sulfur dioxide, the excess of chlorine, and any undecomposed sulfur chloride passed into the trap *A* and thence to the hood.

Using the apparatus fitted with tubes of the dimensions given, at least a kilogram of the chloride could be prepared in an hour and a half.

Reduction of Uranium Chloride by Calcium

About 400 grams of uranium chloride prepared in this manner were mixed with a 10 per cent excess of calcium shavings and placed in the reduction chamber (*C*, Figure 1). This was then placed in the vacuum chamber, and the reaction carried out in the manner described for the reduction of the oxide, the only difference being that the tube was kept in a vertical instead of a horizontal position. Upon opening the reduction chamber, it was seen that a violent action had taken place and the whole mass had fused and run to the bottom. A stream of cold water was allowed to run into the vessel until the slag of calcium chloride had been removed, when the uranium was left in the form of a fused mass. This was carefully detached and examined. The product was found to be much contaminated with iron from the walls of the chamber, which were covered with a bright shining alloy of uranium and iron. Although the product was useless, it showed two things clearly: first, that the temperature of the reaction was sufficiently high to produce the metal in a fused condition; and second, that a lining to protect the metal from iron was necessary.

The next reduction, therefore, was carried out with this last point in view. The reduction chamber was of the type used above, except that it was much larger and fitted with an alundum crucible closed by a cover of the same material.

Owing to the intended increase in the quantity of material undergoing reduction, it became necessary to change the type of apparatus and the method of heating. After approximately twice the quantities of uranium chloride and calcium were placed in the alundum crucible, the crucible was put in the nichrome-wound reduction bomb. This was then placed in the vacuum chamber (Figure 3), which consisted of a steel cylinder approximately 18 inches high and 14 inches in diameter with a welded bottom and a flanged top to which the cover was tightly fitted by means of a gasket and bolts. The connections for electrically heating the bomb were led out through openings *A*, while the opening *B* was connected to two Hyvac pumps. In order to watch the heating and to determine when the reduction took place, a thermocouple was introduced through the opening *C*. To prevent excess radiation an ignited asbestos lining, *D*, around the sides and bottom and an asbestos disk, *E*, over the top of the bomb were used.

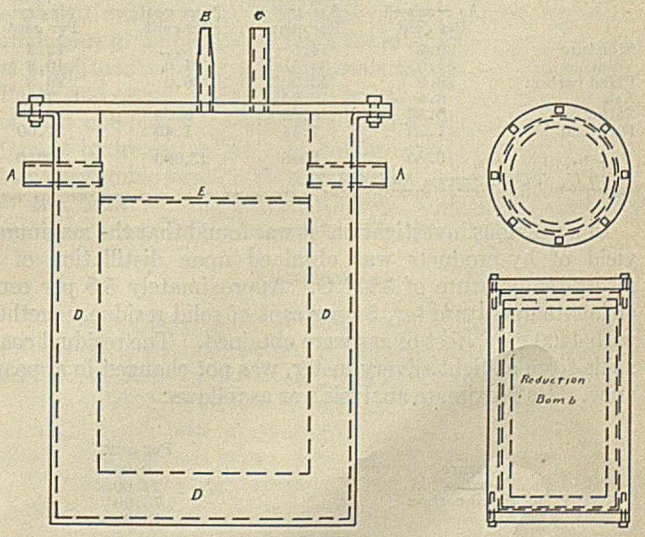


Figure 3

After the cover had been bolted down, connections made, and a vacuum established, the heating current was turned on and the pyrometer readings were noted at equal intervals. When the reduction took place a sharp increase in temperature was observed. After 12 to 24 hours the vessel was opened

and a stream of water run into the crucible to remove the soluble slag. It was found that the uranium had fused into one mass, which was somewhat brittle and hard and not easily worked. A careful analysis made by the highly trained chemists of a reputable company gave the following results:

Uranium	99.31	Silicon	None
Iron	0.57	Calcium	None
Carbon	0.09	Aluminium	Trace
Oxygen	0.03		

This analysis showed the presence of iron and carbon in objectionable quantities.

An examination of the products used indicated that calcium was the source of these impurities. Therefore, to eliminate these substances, the calcium was carefully sublimed before using. While the sublimed calcium itself gave practically no test for iron, the residue contained much iron and carbide.

A similar reduction to the one last described was made using sublimed calcium, with the result that a mass of uranium weighing 1500 grams was obtained. In general, the product resembled the first one except that the ingot possessed a convex surface, was very silvery, and clean, and showed fine crystalline markings. A careful determination showed the iron content to be less than 0.01 per cent.

This same process has been applied with success to the preparation of zirconium, beryllium, and thorium, and plans are being made to test it on vanadium, hafnium, etc.

Effect of Sulfur in the Briquetting of Subbituminous Coal[1]

By H. K. Benson, J. N. Borglin, and R. K. Rourke

University of Washington, Seattle, Wash.

AMONG the subbituminous coals of the State of Washington are some that are more commonly designated as lignites owing to the property of "slacking" or disintegration by weathering. This characteristic has limited the commercial use of such coals and has stimulated experimental studies seeking modifications of structure tending toward greater permanency in form.

In this class is the coal mined at Tono, Washington. It is black in color, with a brown streak, is slightly banded in structure, and breaks with a conchoidal fracture. The proximate analysis of the coal is given in Table I.

Table I—Percentage Composition of Tono Coal

	Car Sample[a]			Laboratory sample
	As received Per cent	Air-dry Per cent	Pure coal Per cent	air-dry Per cent
Moisture	20.2	14.5	..	12.3
Volatiles	31.5	33.5	44.0	40.8
Fixed carbon	39.9	43.9	56.0	39.8
Ash	8.4	9.05	..	7.1
Sulfur	0.52	0.56	0.73	0.3
Nitrogen	1.06	1.14	1.49	1.60
B. t. u.	9280	9940	13,000	9650

[a] *U. S. Geol. Survey, Bull.* **474**, 75.

In a previous investigation[2] it was found that the maximum yield of by-products was obtained upon distillation of a retort temperature of 380° C. Approximately 5.5 per cent of low-temperature tar, 54 per cent of solid residue, together with 4400 cubic feet of gas were obtained. The residual coal, aside from a slight silvery luster, was not changed in appearance. Its proximate analysis was as follows:

	Per cent
Moisture	0.00
Volatiles	14.00
Fixed carbon	73.00
Ash	13.00
B. t. u.	12,710

The general effect of low-temperature distillation resulted in an increase of approximately one-third in heating value, but its physical form was not more favorable for commercial purposes than that of the original coal.

In the present study an attempt was made in a preliminary way to modify the structure of Tono coal, so that its fuel values and its form and structure might alike enhance its commercial use. Attention was directed to the action of sulfur as a temporary intermediate agent in the coking of coal, and various mixtures of sulfur, asphaltic binder, and Tono coal were heated to 700°–950° C. for the purpose of forming a coke-like mass.

Experimental

The coal was ground to pass 20 mesh and then mixed with pulverized, crude sulfur in varying proportions. This mixture was then poured into molten asphalt obtained from a local briquetting plant, thoroughly stirred until a uniform plastic mass was obtained, and then compressed in a hydraulic press into briquets 3 cm. (1.25 inches) in diameter and 5 cm. (2 inches) long. The briquets were carbonized in cast-iron retorts for 8 hours at temperatures of 700° to 950° C. Some runs were allowed to cool in the retort while others were quenched with water.

Experiment I

Table II—Sulfur and Tono Coal

Run	Sulfur in mixture Per cent	Sulfur in residue Per cent	Remarks
	Temperature, 700° C.		
1	1.00	1.79	No coking
2	1.96	2.00	
3	2.90	2.19	
4	3.84	2.94	
5	9.10	3.67	
	Temperature, 950° C.		
6	1.95	1.95	
7	4.75	2.45	
8	6.52	3.57	
9	9.10	6.80	

To ascertain the effect of the asphaltic binder, briquets containing 5, 10, 15, and 35 per cent, but no sulfur, were carbonized under the same conditions as above. The residue crumbled under pressure between the fingers.

Experiment II

To ascertain the effect of briquetting, a batch was divided into two parts, one distilled unbriquetted and the other briquetted. (Table III)

[1] Presented by H. K. Benson and J. N. Borglin before the joint session of the Division of Petroleum Chemistry and the Section of Gas and Fuel Chemistry at the 70th Meeting of the American Chemical Society, Los Angeles, Calif., August 3 to 8, 1925.

[2] Benson and Davis, This Journal, **9**, 946 (1917).

Table III—Sulfur, Tono Coal, and Asphalt

Run	Binder Per cent	Sulfur in mixture Per cent	Sulfur in residue Per cent	Remarks
		Unbriquetted		
1	4.55	5.35	3.60	Slight coking
2	12.47	4.90	3.55	Hard coke
3	19.20	3.84	3.48	
4	25.00	3.57	3.40	
		Briquetted		
1	4.55	5.35	2.21	Fair coke
2	12.45	4.90	1.95	Hard coke
3	19.20	3.84	1.81	Fused mass
4	25.00	3.57	1.23	

Experiment III

The effect of varying the original content of sulfur with approximately the same quantity of binder is shown in Table IV.

Table IV—Sulfur Content of Coke Residues

Run	Binder Per cent	Sulfur in mixture Per cent	Sulfur in coke residue Per cent
1	4.63	3.64	2.36
2	4.36	9.43	2.52
3	12.73	3.33	2.15
4	12.00	8.68	2.24
5	19.55	3.03	1.60
6	18.50	8.03	1.93
7	26.30	2.81	1.35
8	24.18	7.48	1.83

Experiment IV

The addition of sulfur to binder alone yielded a coke of fragile character. The results are given in Table V.

Table V—Carbonization of Sulfur-Asphalt Mixtures at 950° C.

Run	Sulfur in mixture Per cent	Sulfur in residue Per cent	Loss in weight Per cent	Remarks
1	3	1.25	75	Very friable
2	5	1.45	85	
3	7	1.90	86	
4	10	2.38	80	

Experiment V

The desulfurization of coke made at 950° and 700° C., respectively, by quenching in water, is shown in Table VI.

Table VI—Effect of Quenching Coke in Water

Run	Binder Per cent	Sulfur in mixture Per cent	Sulfur in air-cooled coke Per cent	Sulfur in quenched coke Per cent
1	4.63	3.64	2.36	1.51
2	12.73	3.33	2.15	1.39
3	19.55	3.03	1.60	1.49
4	26.30	2.81	1.35	1.79

Burning Tests

A number of the carbonized briquets were placed in a small pot furnace and burned with a forced draft. They gave an intensely hot fire and held their shape until they were completely consumed.

Two lots of briquets, one containing 8 per cent binder and 3 per cent sulfur, and the other containing the same amount of binder but no sulfur, were burned without forced draft. Those containing sulfur held their shape and tended to increase in strength as they burned, while those containing no sulfur fell to pieces. Figure 1 shows the difference in the behavior of these two briquets.

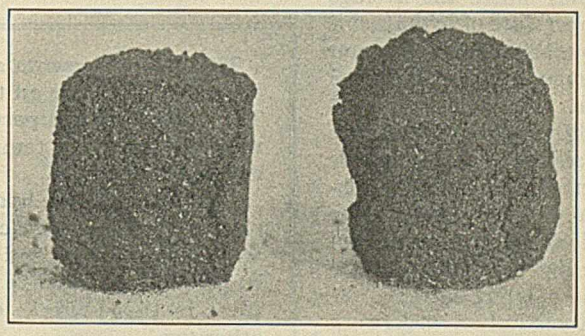
Discussion of Experimental Results

From Table II it is seen that the various mixtures of sulfur and Tono coal and of asphalt and Tono coal yielded no coke-like mass upon carbonization at 950° C. Upon the addition of 3 to 5 per cent sulfur to Tono coal containing from 5 to 25 per cent asphalt, a hard coke resulted (Table III). This action is especially noticeable in the briquets in the pot furnace, those containing as little as 3 per cent sulfur holding their shape while those with asphalt binder alone lost their shape completely during the burning. This same distinction also applies to the strength and ability of the carbonized briquets to withstand shock, enabling them to be handled without abrasion while those carbonized without sulfur were readily disintegrated by slight pressure.

The lower temperature of carbonization—i. e., at 700° C.—did not seem to affect the character of the residue either in its sulfur content or in its physical properties, provided the carbonization was carried to completion. The effect of quenching was very evident in the reduction of sulfur content of the residue.

Theoretical Discussion

The experimental work above noted is not sufficiently exhaustive in character to permit definite conclusions, and the investigation is being continued in the form of a sulfur survey of all the products of carbonization. A number of explanations might, however, be advanced to account for the coking effects.



Without sulfur With sulfur

Figure 1—Partially Burned Briquets

The action of sulfur on paraffin is well known.[3] Very recently[4] this mixture has been recommended as a convenient source of hydrogen sulfide for student use. Apparently sulfur reacts on paraffin by withdrawing hydrogen from the hydrocarbons to form hydrogen sulfide and resulting in a more condensed hydrocarbon molecule. Powell[5] has shown, however, that the similar residue in coke is a solid solution of sulfur in carbon. Whatever mechanism sulfur brings about, it evidently produces a physical structure somewhat analogous to that obtained from the interaction of two classes of constituents found in coking coals as held by Illingworth,[6] Parr,[7] and others. Powell[8] also points out that in the coking of coal one-fourth to one-third of the organic sulfur is set free as hydrogen sulfide, the balance remaining in the coke as a very stable carbon sulfur combination, highly reminiscent of the behavior of nitrogen whereby a very stable carbon nitrogen compound remains behind in the coke.

Conclusions

1—The carbonization at 700° to 950° C. of a mixture containing 3 per cent sulfur, 8 per cent California asphalt, and 89 per cent Tono coal will yield a firm, coke-like mass.

2—The sulfur content of the carbonized residue will be about 2.25 per cent when allowed to cool in the retort, and about 1.40 per cent when quenched in water.

3—Such carbonized masses, when burned with a forced draft hold their shape until entirely consumed.

4—A mixture of 3 per cent sulfur, 8 per cent California asphalt, and 89 per cent Tono coal can be made into briquets which, without previous carbonization, will hold their shape while burning.

[3] *U. S. Geol. Survey, Bull.* **770**, 739.
[4] *J. Franklin Inst.*, **199**, 5, 685 (1925).
[5] *J. Am. Chem. Soc.*, **45**, 1 (1923).
[6] *J. Soc. Chem. Ind.*, **39**, 111, 133 (1920).
[7] *Trans. Ill. State Acad. Sci.*, **15**, 352 (1922).
[8] *Am. Gas Assoc., Tech. Sec. Sessions*, **2**, 244 (1920).

The Hydration of Lime[1]

By W. G. Whitman and G. H. B. Davis

Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Mass.

This paper presents a study of the effect of various hydration methods on the properties of hydrated lime. The three most important variables are the ratio of water to lime, the temperature of hydration, and the degree of agitation.

The quality of the hydrated product was evaluated by testing its rate of reaction with acid and its rate of settling in water and by microscopic examination. In general, the relative rating of quality by any one of these methods checks closely with the ratings by the other two.

The best product was prepared by hydrating quicklime with a large excess of water in boiling solution. Hydration with the theoretical amount of water or with water vapor gave a coarse inferior hydrate.

The literature covering the influence of the method of hydration of lime upon the quality of the product is sparse and somewhat inconclusive. Bachtenkercher[2] attempted to show that hydrated lime exists in two different forms—a fine amorphous form, stable at ordinary temperatures, and a coarse crystalline one, which is produced when the temperature of hydration rises above 180° F. Although his "crystalline and amorphous" theory was disproved by Latham,[3] he did show that lime which is hydrated under conditions where the average temperature of hydration is above 180° F. yields a poorer product (larger particles) than that hydrated at slightly lower temperatures. He also showed that there is a certain amount of flocculation of the hydrated lime and made an unsuccessful attempt to find a suitable deflocculating agent.

Kohlschutter,[4] in his work on rates of settling, showed that calcium hydroxide prepared by adding water to lime was coarser and settled more rapidly than that prepared by adding lime to water.

Holmes, Fink, and Mathers,[5] working likewise on rates of sedimentation, showed that lime hydrated with excess water was finer and settled more slowly than if only the theoretical amount was used. These investigators also concluded that (*a*) the lower the temperature of hydration the finer the product, (*b*) freshly slaked lime is finer than the commercial hydrate, and (*c*) the slaked lime will settle more slowly if it is allowed to stand in contact with water for some time.

Preparation of Samples

Twelve samples of hydrated lime were prepared from a single sample of quicklime by the various methods described below. The master sample was an Ohio quicklime described as a quick-slaking, high-calcium, porous lime. The different methods of preparation were designed to show the effects of (*a*) the physical state of the water (vapor or liquid), (*b*) the proportions of water to lime, (*c*) the temperature, and (*d*) the degree of agitation. A sample of commercial hydrate from the same quicklime was tested in parallel with the prepared hydrates.

The quicklime was broken up in a mortar until there were no lumps larger than 0.5 cm. Twenty-five grams of this were then used for each preparation.

Hydration with Theoretical Amount of Water—(*a*) *At 30° C.* The lime was placed in a small evaporating dish and cold water was added gradually until the theoretical amount was reached. The mass was stirred with a thermometer and the water was added at such a rate that the temperature at no time exceeded 40° C.

(*b*) *At 100° C.* Warm water, 30 per cent in excess of the theoretical amount to take care of evaporation, was added rapidly to the lime. The temperature rose quickly and steam was generated. When the product was dry any unhydrated lumps were screened off.

Hydration with Water Vapor—(*a*) *At 30° C.* The dry lime was placed on a watch glass in a desiccator over water and allowed to stand for 3 weeks at 30° C.

(*b*) *At 100° C.* Dry steam was passed over the lime for 2 hours. The powder was then screened to remove any unhydrated lime.

(*c*) *At 250° C.* The lime was sealed in a heavy glass tube wrapped with a spiral of chromel wire and suspended above water in an autoclave. When the autoclave had been heated until the pressure gage read 40 atmospheres the glass tube was shattered by heating the chromel wire electrically. The lime which remained with the glass fragments in the wire spiral then hydrated by contact with water vapor.

Hydration with Five Times Theoretical Water—(*a*) *At 30° C.* The lime was added to five times the theoretical amount of water in a beaker in a water bath kept at 30° C.

(*b*) *At 100° C.* The procedure was the same as in the previous preparation except that the lime was added to boiling water.

Hydration with Twenty Times Theoretical Water—(*a*) *At 30° C.* The lime was added to twenty times the theoretical amount of water in a beaker in a water bath at 30° C.

(*b*) *At 100° C. but not boiling.* The water was placed in an autoclave with 50 cc. of petroleum ether and lime, sealed in a glass tube suspended above the liquid. After closing the autoclave it was heated in a pail of boiling water for half an hour. Then the tube containing the lime was broken by passing an electric current through a wire around the tube, thus allowing the lime to fall into the water. The water was kept from boiling by the pressure exerted by the petroleum ether.

(*c*) *At 250° C.* Twenty times the theoretical amount of water was placed in the autoclave and the lime sealed in a glass tube suspended above it. The autoclave was heated till the gage showed 40 atmospheres pressure corresponding to about 250° C. The tube containing the lime was then broken, allowing the lime to fall into the water.

(*d*) *At 60° C. and boiling.* The lime was added to twenty times the theoretical amount of water at 50° C. in a vacuum desiccator. The pump was turned on and the liquid boiled violently. When the reaction was over the temperature had risen to 60° C.

(*e*) *At 100° C. and boiling.* The lime was added to twenty times the theoretical amount of boiling water.

Commercially Hydrated Lime—This was a sample of commercial hydrate made from the same quicklime as was used for the master sample.

Tests on Product

The methods for determining relative particle size are based on three tests: rate of reaction, rate of settling, and microscopic examination.

The rate of reaction was determined by adding 10 cc. of 1 *N* hydrochloric acid rapidly to a suspension of the hydrate which contained phenolphthalein and timing with a decimal stopwatch the interval before the reappearance of the pink color. The suspension contained 3.7 grams of hydrate (0.1 equivalent)

[1] Received November 18, 1925.

[2] *Lime Lights*, **1908**, 223; **1909**, 337; *Trans. Nat. Lime Assoc.*, **1910**, 73; **1911**, 209; *Chem. Eng.*, **18**, 189 (1914).

[3] *Concrete-Cement Age*, **6**, Cement Mill Section 9 (1915).

[4] *Z. Elektrochem.*, **25**, 159 (1919).

[5] *Chem. Met. Eng.*, **27**, 1212 (1922).

Table I—Time for Reaction with Acid (in 0.01 Minute)

Method of Preparation	Recorded Time to Neutralize Each Successive 10 Cc. of Acid										Total Time (Cor.) to Neutralize Indicated Number of 10-Cc. Portions of Acid									
	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	1st	2nd	3rd	4th	5th	6th	7th	8th	9th	10th
Theoretical:																				
30° C.	0	1	4	8	13	18	25	36	70	Over 450	0	0.3	1.3	2.9	5.1	7.7	10.8	14.8	21.8	...
100° C.	3	5	9	17	22	26	33	52	87	Over 450	1.5	3.2	5.4	8.8	12.4	16.1	20.2	25.9	34.6	...
Vapor:																				
30° C.	1	2	4	6	8	20	29	47	70	Over 450	0.5	1.2	2.2	3.4	4.7	7.6	11.2	16.4	23.0	...
100° C.	1	3	5	9	12	20	32	55	97	Over 450	0.5	1.5	2.7	4.5	6.5	9.4	13.4	19.5	29.2	...
250° C.	0	0	1	2	6	15	30	60	183	Over 450	0	0	0.2	0.6	1.6	3.7	7.5	14.2	32.5	...
Five times theoretical:																				
30° C.	0	0	1	3	9	19	17	26	55	Over 450	0	0	0.2	0.8	2.3	5.0	7.1	10.0	15.5	...
100° C. with boiling	0	0	0	1	2	5	9	15	82	Over 450	0	0	0	0.2	0.5	1.2	2.3	4.0	12.2	...
Twenty times theoretical:																				
30° C.	0	0	1	2	7	12	15	22	56	Over 450	0	0	0.2	0.6	1.8	3.5	5.4	7.8	13.4	...
100° C.	0	0	1	2	5	9	14	25	40	Over 450	0	0	0.2	0.6	1.4	2.7	4.5	7.2	11.2	...
250° C.	0	0	1	2	3	6	12	30	82	Over 450	0	0	0.2	0.6	1.1	2.0	3.5	6.8	15.0	...
60° C. with boiling	0	0	1	2	5	9	14	21	77	Over 450	0	0	0.2	0.6	1.4	2.7	4.5	6.8	14.5	...
100° C. boiling	0	0	0	0	1	2	4	8	16	Over 450	0	0	0	0	0.1	0.4	0.9	1.8	3.4	...
Commercial product	0	1	2	6	14	28	50	81	212	Over 450	0	0.3	0.8	1.9	4.2	8.2	14.4	23.4	44.6	...

diluted with water to 10 cc. and the 10-cc. dose of acid was repeated ten times to completely neutralize the lime.

Table I gives the original data on the times required for the reaction with each of the ten successive batches of acid. A second set of figures in this table gives the total corrected times for reaction, calculated on the assumption that the time is inversely proportional to the initial concentration of acid in the suspension. Thus, when 10 cc. of 1 N acid are added to 20 cc. of suspension, the initial concentration of acid in the mixture is $N/3$ and the observed time is corrected by multiplying by $^1/_3$. The figure for total corrected time is obtained by summing up the corrected times for the individual additions. Figure 1 shows a few typical curves of the total corrected time required to dissolve varying percentages of the lime.

The rates of settling were determined by the method employed by Holmes, Fink, and Mathers[5] in which 10 grams of hydrated lime were placed in a 100-cc. graduate (2.58 cm. internal diameter) filled to the 100-cc. mark, shaken well, and allowed to settle, readings being taken every 5 minutes. Table II gives these data as per cent of the total volume occupied by the suspension after various time intervals, and Figure 2 illustrates the type of curves obtained on a few of the hydrates.

Table II—Data on Rate of Settling of Lime Suspensions

Time in minutes	5	10	15	20	30	60	110	1200
Vapor:								
30° C.	79	60	43	28	25	22.1	22	21.9
100° C.	74	50	32	26	23	21.5	21.4	21.0
Twenty times theoretical:								
30° C.	80	64	47.5	41	29	25	23.9	23.9
100° C.	94	88	80	72	60	38.5	34.5	31.0
250° C.	94.5	90	84	79	68.6	47.5	41.8	30.9
60° C. with boiling	92	86	78	69	51	31	29.6	27.5
100° C. with boiling	98	97	95.5	94.3	91.6	83.5	70.2	35.0
Commercial product	83	73	62	54	41	29	28.9	28.8

The microscopic tests are difficult to show clearly. Table III gives a summary of the results, while Figure 3 shows sample drawings of the different types of clusters.

Table III—Results of Microscopic Examination

Type of Cluster	Sample
Large and tight	Theoretical at 30° C. Theoretical at 100° C. Vapor at 30° C. Vapor at 100° C. Vapor at 250° C.
Small and very tight	Commercial
Small and tight	Five times theoretical at 30° C. Twenty times theoretical at 30° C. Twenty times theoretical at 100° C. not boiling Twenty times theoretical at 250° C.
Small, some tight, some loose	Twenty times theoretical boiling at 60° C.
Small and loose	Five times theoretical, boiling at 100° C. Twenty times theoretical, boiling at 100° C.

Discussion

Table IV summarizes the results of the three tests, showing the total corrected times to dissolve 80 per cent of the various samples, the depths of settling in 15 minutes, and the microscopic observations.

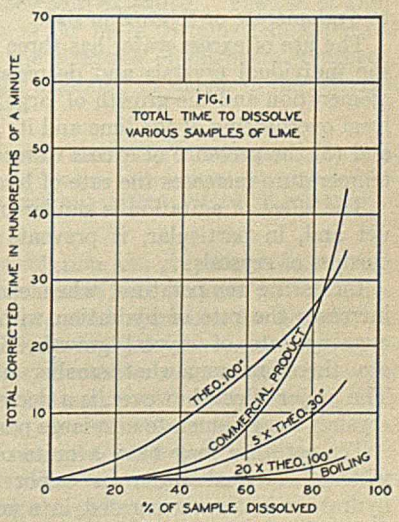
Table IV—Summary of Results

Sample	Total cor. time to dissolve 80% Min.	Depth of settling in 15 min. Cm.	Type of Clusters
Theoretical:			
30° C.	14.8	..	Large
100° C.	25.9	..	Large
Vapor:			
30° C.	16.4	68	Large
100° C.	19.5	57	Large
250° C.	14.2	..	Large
Five times theoretical:			
30° C.	10.0	..	Small tight
100° C. boiling	4.0	..	Small loose
Twenty times theoretical:			
30° C.	7.8	52	Small tight
100° C. no boiling	7.2	20	Small tight
250° C.	6.8	16	Small tight
60° C. boiling	6.8	22	Small loose
100° C. boiling	1.8	4	Small loose
Commercial hydrate	23.4	38	Small very tight

The time required for reaction as given in Table IV is a function of the surface area of the hydrate and may be used as an "index" of the size of the individual particles.

Note—The proportions of particles of various sizes in the sample may be calculated from the data on the rate of solution in hydrochloric acid by making the following assumptions: (1) The particles are all of uniform shape and not clustered; and (2) the number of particles remains constant during any one addition of acid. These calculations would be similar to those of Murphree[6] on the rate of solution of crystals.

Using this index the following comparisons may be drawn:



1—The use of excess water produces a hydrate which is much finer than that obtained by reaction with theoretical water or with vapor. Thus the index numbers are all below 10 when excess water is employed, and are above 10 for all other samples, including the commercial hydrate. Increasing the excess water from five to twenty times the theoretical increases the fineness of the hydrate to a small degree.

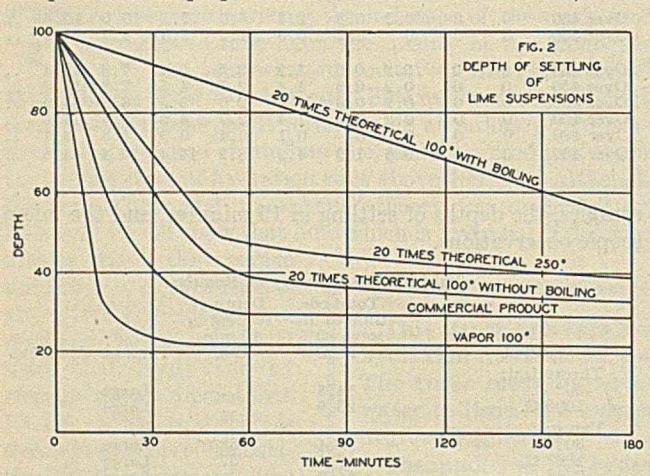
2—Boiling markedly increases fineness.

3—Increasing temperature increases fineness to a slight extent when excess water is employed. This is noticeable in the runs with twenty times the theoretical water at 30°, 100°, and 250° C. without boiling. Increasing temperature gives a poorer product, however, when theoretical water or water vapor is used. The run with vapor at 250° C. is an exception which will be discussed later.

[6] This Journal, 15, 148 (1923).

4—Vapor hydration gives about the same results as are obtained with theoretical water. The commercial hydrate corresponds in particle size to vapor or theoretical water hydration at 100° C.

The data on rate of settling lead to somewhat parallel conclusions. Thus, excess water and boiling produce hydrates which have slow settling rates. However, the effect of temperature of preparation is much more marked, as illustrated by the rapid settling of the sample prepared at 30° C. with twenty times the theoretical water. This hydrate settles even more rapidly than the commercial product, although it has a much larger surface area as determined by its rate of reaction.



The essential difference between these two tests is that the reaction rate is a function of surface area while the settling rate is determined by the size of agglomerates of particles. Thus, a hydrate which consisted of very fine particles would react rapidly with acid, but these particles might be clustered together in lumps which would settle rapidly. Such seems to be the case when lime is slowly hydrated at low temperatures with excess water.

The explanation of all these results may be deduced from a general principle that fine particles are produced by rapid hydration when there is little opportunity for the crystals to agglomerate or to grow in size.

The use of excess water has three effects: (1) it separates the individual crystals and decreases the tendency for agglomeration and the growth of large crystals; (2) it prevents local overheating of the lime and its resulting disadvantages; and (3) the presence of excess water at any definite uniform temperature increases the rate of hydration.

The effect of agitation is similar in producing a fine product and, in particular, it prevents the formation of tight clusters of crystals.

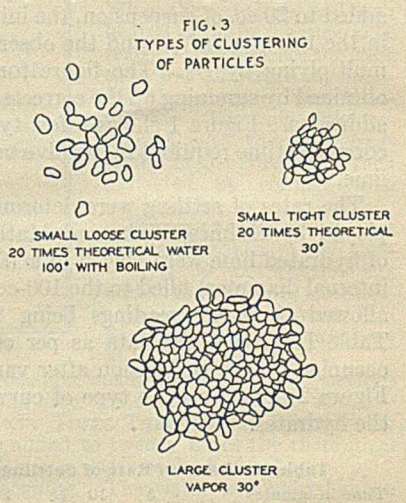
Increasing temperature, when excess water is employed, increases the rate of hydration without correspondingly increasing rate of crystal growth. The individual crystals are therefore somewhat smaller at higher temperatures. The major effect, however, is a decreased tendency for small crystals to agglomerate into large particles.

Temperature may have a quite opposite effect, however, when theoretical water or vapor is used. The heat of hydration is then generated in a mass of such small heat capacity that the temperature rises rapidly, causing overheating or "burning" and producing a coarse and inferior product. To illustrate this, a thermocouple was inserted in a hole drilled in a large lump of quicklime. The lime was placed in a dish partly filled with water so that the steam resulting from hydration of the lower part would hydrate the upper part. In this experiment a thermocouple temperature of 465° C. (869° F.) was recorded.

Johnston's data[7] show that lime cannot be hydrated at atmospheric pressure at temperatures above 547° C. (1017° F.) and that at this temperature hydrated lime will lose its water and dehydrate unless put under pressure. "Burning" temperatures evidently approach this dehydrating point, and therefore the rate of hydration in any part of the mass which has been raised to such high temperatures will be very slow. Practically, if a particle of quicklime is brought up to the dehydrating point by the heat evolved around it, that particle cannot hydrate until enough heat has been lost to lower the temperature. As a result, the rate of further hydration will be determined by the rate of heat loss and this latter would be relatively slow in a lump of quicklime in the center of the hydrating mass. Such a slow rate of hydration would give large particles. It is believed that the deleterious results of "burning" during hydration are adequately explained by this concept.

If the lime is hydrated under pressure the dehydrating temperature is increased by an amount which depends upon the pressure. Thus, quicklime initially at 250° C. has been hydrated by vapor at 40 atmospheres pressure, and the product was even better than that obtained when lime initially at 100° C. was hydrated by vapor at atmospheric pressure.

In the usual type of commercial hydrator the lime, with a slight excess of water, is fed into a system of cylinders and carried through by screw conveyors, being discharged as a hot, dry, powdered hydrate. Thus, although the lime is at first partially hydrated with excess water, this water rapidly changes to steam and the remainder is hydrated by vapor. As has been shown, hydration with only a slight excess of water or with steam yields a relatively coarse product.



The superiority of slaked lime properly prepared in a mortar box over commercial hydrate is due primarily to the large excess of water. It is probable that the average slaking operation employs an excess corresponding to five times the theoretical amount of water.

Conclusions

High-grade hydrate contains many fine particles which are produced when the rate of hydration is rapid compared with the rate of growth of the particles. Conversely, inferior coarse hydrate is formed when the rate of hydration is slow and time is allowed for crystal growth. Excess water, reasonably high temperatures, and agitation all favor rapid hydration and a fine product.

Excessively high temperatures, generated locally in the lime from the heat of reaction, are very detrimental because the lime approaches its "dehydrating" temperature while still only partially hydrated. Completion of the reaction is then very slow since the lime must lose heat before hydration can continue. During this time the particles have a chance to grow in size and the final product is very coarse. An elimination of conditions which produce these effects would undoubtedly result in an improvement in the quality of most commercial hydrates.

[7] *Z. phys. Chem.*, **62**, 330 (1908)

Successive Potentiometric Titration of Copper and Iron in Metallurgical Products[1]

By Theo. F. Buehrer and O. E. Schupp, Jr.

University of Arizona, Tucson, Ariz.

In order to eliminate the necessity of separating copper from iron in analytical procedure, as is now generally required by all the accepted gravimetric and volumetric methods owing to the similarity of their properties in the dissolved state, the successive potentiometric titration of these elements has been studied. Both direct and indirect methods of titration involving reduction with stannous or titanous chloride have been found unsatisfactory. When chromous chloride is used as the reducing agent, either by direct titration or by residual titration with dichromate, the determination of copper and iron, both singly and in their mixtures, is both accurate and rapid. When applied to certain copper smelter products, the methods involving chromous chloride can be recommended in point of accuracy, simplicity, and economy of time, expense, and effort. The reactions involved are deduced on the basis of standard molal reduction potentials of the ions in question, and sources of error in each case are discussed.

SINCE the reactions of copper and iron in solution are very similar, the accurate determination of either of these elements by means of the accepted gravimetric or volumetric methods presupposes a separation of one from the other, and such separation is, as a rule, time consuming. Potentiometric methods have in recent years been applied individually to copper[2] and iron,[3] but the writers have found only the work of Tomicek[4] and Kolthoff[5] on the successive electrometric titration of these two elements, which will be discussed later in this paper.

Since the potentiometric method for iron alone is sufficiently well established, it was considered best to confine the attention in this paper to the study of copper alone and of copper-iron mixtures. As above stated, the properties of copper and iron in solution present a number of similarities: they both form insoluble hydroxides, sulfides, ferrocyanides, and complex chloro ions; they also occur in two stages of oxidation. Preliminary experiments showed that the precipitation method would be out of the question, but that a suitable oxidation or reduction method might be feasible. Table I[6] was used as a basis of choosing conditions and reagents.

Table I—Molal Reduction Potentials of Certain Ions and Metals

		Volt
$Cr^{++} \longrightarrow$	Cr^{+++}	+0.43
$Ti^{+++} \longrightarrow$	Ti^{++++}	+0.00
$H_2 \longrightarrow$	H^+	0.00
$Sn^{++} \longrightarrow$	Sn^{++++}	−0.14
$Cu^+ \longrightarrow$	Cu^{++}	−0.17
$Hg_2Cl_2 \longrightarrow$	Hg^{++}	−0.24
$Cu^\circ \longrightarrow$	Cu^+	−0.34
$Fe^{++} \longrightarrow$	Fe^{+++}	−0.75
$Cr^{+++} \longrightarrow$	$HCrO_4^-$	−1.3

On the basis of these reduction potentials, a study of the problem was planned from the following points of view:

1—Complete reduction followed by titration with standard dichromate
- (*a*) $SnCl_2$-$HgCl_2$ combination as in Penny's method
- (*b*) Excess $SnCl_2$ added and titration with dichromate
- (*c*) Excess $TiCl_3$ added and titration with dichromate
- (*d*) Excess $CrCl_2$ added and titration with dichromate

2—Direct electrometric titration with standard reducing agents
- (*a*) Stannous chloride
- (*b*) Titanous chloride
- (*c*) Chromous chloride

Preparation of Materials

The copper chloride solution was prepared from C. P. copper wire by dissolving in nitric acid, removing the excess nitric acid completely by evaporating to dryness with an excess of concentrated hydrochloric acid, and heating the dry salt on the hot plate until brown fumes were no longer given off. The hydrochloric acid solution of this salt was standardized both volumetrically and electrolytically. The iron solution was made up from ferric chloride, which was tested and found free from reducible impurities. It was standardized both volumetrically by Penny's method and potentiometrically. Samples of these solutions were weighed out from a weight pipet. The potentiometric titration unit was of the Hostetter and Roberts type, in combination with platinum and calomel electrodes. The solution was stirred vigorously by means of a mechanical stirrer. To exclude atmospheric oxygen, a layer of kerosene about an inch deep was placed over the solution, through which the stirrer, buret tip, and electrodes extended. The use of kerosene for excluding air was far more certain than the usual method of titrating in the presence of nitrogen, hydrogen, or carbon dioxide, and the solubility of the air in the kerosene appeared to be negligible.

Note—P. S. Danner states that unsaturated hydrocarbons in kerosene greatly increase the solubility of oxygen, and suggests that they be first removed by successive treatment with several changes of concentrated sulfuric acid.

The stannous chloride solution was prepared from crystalline salt and the titanous chloride from a 15 per cent solution. Chromous chloride was prepared according to Evans,[7] by boiling potassium dichromate in hydrochloric acid solution with a considerable excess of arsenic- and iron-free zinc until reduction to the light blue solution was complete. This solution was immediately covered with a layer of kerosene and transferred to the reagent bottle by pipetting under kerosene. It was standardized very easily against standard dichromate solution using the potentiometric indicator (Figure 1). Although extremely sensitive to oxygen, as Table II will show, the solution was found to maintain a fairly constant normality.

Table II—Stability of Chromous Chloride Solution

Days	0	1	3	4	5.5	6.5	8
Normality	0.0927	0.0921	0.0923	0.0919	0.0919	0.0918	0.0916

[1] Presented under the title "The Successive Electrometric Titration of Copper and Iron in Metallurgical Products" before the joint session of the Divisions of Industrial and Engineering Chemistry and Cellulose Chemistry and the Section of Paint and Varnish Chemistry at the 70th Meeting of the American Chemical Society, Los Angeles, Calif., August 3 to 8, 1925.

[2] Zintl and Wattenberg, *Ber.*, **55**, 3366 (1922); Willard and Fenwick, *J. Am. Chem. Soc.*, **41**, 1337 (1919).

[3] Hildebrand, *Ibid.*, **35**, 869 (1913); Hostetter and Roberts, *Ibid.*, **41**, 1337 (1919).

[4] *Rec. trav. chim.*, **43**, 800, 812 (1924).

[5] *Ibid.*, **43**, 820 (1924).

[6] Treadwell-Hall, "Qualitative Analysis," Vol. I, **1921**, p. 44; Gerke, *Chem. Rev.*, **1**, 377 (1925).

[7] "Metals and Metallic Compounds," Vol. II, p. 304.

In standardizing the dichromate solution, concordant results were obtained only by employing as a standard the Sibley Iron Ore No. 27 of the United States Bureau of Standards.

Titration with Potassium Dichromate after Reduction with Various Reducing Agents

Stannous-Mercuric Chloride

The procedure of Penny's method for iron was first tried out on copper alone. From the reduction potentials it was regarded as a foregone conclusion (*a*) that copper would hardly be reduced completely by stannous chloride, and (*b*) that cuprous ion would react with mercuric ion present. Both of these factors would lead to low results for copper. Experiments showed, in fact, that while the titration curves were satisfactory the results were uniformly low in amounts varying from 0.4 to 12.0 per cent. Conditions of concentration, acidity, volume of stannous chloride used for reduction, and amount of mercuric chloride solution used for removal of excess stannous were varied over wide limits. As to completeness of the reduction with stannous chloride, the discharge of the intense olive green solution of cupric chloride acidified with hydrochloric acid to a perfectly water white solution is believed to be evidence of complete reduction to chlorocuprous acid, $H_2Cu_2Cl_4$. The low results must therefore be attributed to reaction of the chlorocuprous acid with the mercuric chloride. This was proved by allowing the solution, after reduction, to stand different periods of time in the presence of excess mercuric chloride. The results obtained are shown in Table III.

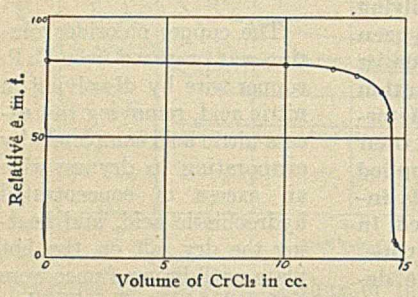


Figure 1—Titration of Potassium Dichromate by Chromous Chloride in Standardizing Chromous Chloride

Table III—Effect of Mercuric Chloride on Chlorocuprous Acid

Cu taken Gram	Time of standing Minutes	Cu found Gram	Per cent error
0.1009	55	0.0846	−16.2
0.1018	90	0.0800	−21.3
0.0977	115	0.0709	−27.4

This observation precluded the use of the stannous-mercuric combination, except for the case of very low acidity where the cuprous chloride precipitates out: $H_2Cu_2Cl_4 = 2CuCl + 2HCl$. Although under this condition the rate of reaction with mercuric chloride is greatly decreased, the titration of the solid cuprous chloride is rendered impracticable, because the reaction is too slow.

To overcome this difficulty and yet be able to use stannous chloride for reduction, it was considered desirable to eliminate the mercuric chloride entirely and to titrate selectively the excess of stannous ion present. This, however, was unsuccessful, because the oxidation potentials of cuprous and stannous ion are practically equal, so that only one inflection point was obtained in the titration curve corresponding to the simultaneous oxidation of both.

Titanous Chloride

The method of Zintl and Wattenberg,[2] who first reduce with excess titanous chloride, followed by titration selectively with potassium dichromate, was also studied in this connection with a view of applying it to the determination of both iron and copper. When applied to iron it yielded absolutely the same results as are obtained by other standard methods. In the case of copper, however, for which they claim accuracy and reliability over widely varying conditions, the writers not only failed to confirm their work, but found considerable positive or negative variations. Determinations made under identical conditions, for instance, did not agree, as shown in Table IV.

Table IV—Titration of Copper with Dichromate after Reduction with Titanous Chloride

Volume of soln. Cc.	Per cent HCl	Temperature ° C.	Cu taken Gram	Cu found Gram	Per cent error
70	11	30	0.1330	0.1320	−0.7
70	11	30	0.1319	0.1317	−0.2
25	30	30	0.0772	0.0790	+2.3
25	30	80	0.0766	0.0784	+2.3
70	10	30	0.1363	0.1357	−0.44
50	10	30	0.1383	0.1389	+0.43
200	7	80	0.0873	0.0841	−3.6
200	4	80	0.0755	0.0710	−6.3

In this connection it may be pointed out that, as indicated under Preparation of Materials, special tests were conducted to make certain that there were no reducible impurities in the copper solutions, such as iron or arsenic, which would be calculated as copper. Most of the results for copper by this method were low. Additional series of analyses on copper and copper-iron mixtures have shown both the direct and the indirect reductions with titanous chloride alone to be incomplete, so that this solution cannot be used in this connection.

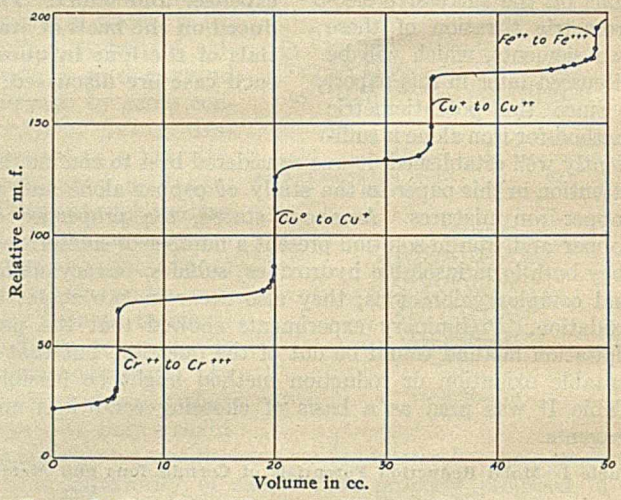


Figure 2—Titration of Copper and Iron by Dichromate after Reduction with Chromous Chloride

Note—Comment of reviewer of this article: "Failure to make such a correction (that is, for the amount of iron present in the titanous chloride solution itself) could account for the positive errors in Table IV, but not for the negative ones. The fact that exact results were obtained for iron seems to rule out this possible explanation of the high results." The writers did, in fact, find a trace of iron, so small in amount as to have no effect on the results. The variations are, no doubt, inherent in the fundamental titration reaction.

Chromous Chloride

The apparent failure of the preceding experiments indicated that selective electrometric titration of the copper and excess reducing agent were probably due to the reduction potentials of both stannous ion and titanous ion being very nearly equal to that of cuprous ion. Therefore an even stronger ionic reducing agent was sought which would make this possible. Chromous, molybdous, and vanadous salts are all powerful reducing agents. Chromous chloride being the most desirable one from the simplicity of its oxidation to chromic ion without intermediate steps, experiments were

carried out as above with marked success. Chromous chloride has a reduction potential (Table I) against hydrogen of +0.43 volts, and it is generally regarded as the most powerful ionic reducing agent. It liberates metallic silver, copper, mercury, lead, and even hydrogen from their ions, and reacts instantaneously with oxygen, for which reason it has been used in gas analysis. The method of preparation and handling of the solution has been given earlier in this paper.

Chromous chloride reduces cupric ion first to cuprous ion, and with the addition of more chromous ion, to finely divided metallic copper. On titrating potentiometrically with dichromate, three inflections are obtained in the e. m. f.–volume curve, corresponding, respectively, to the oxidations Cr^{++} to Cr^{+++}, Cu° to Cu^{+}, and Cu^{+} to Cu^{++}. The differences of potential between these points are sufficiently great to yield definitely distinguishable inflection points. Several possible reactions may take place during the dichromate titration. For example, metallic copper may be oxidized directly to cupric ion, but the equilibrium constant of the reaction $Cu^{\circ} + Cu^{++} = 2Cu^{+}$ is so great that as soon as cupric copper appears it is immediately reduced. Also, if ferrous ion should momentarily be oxidized to ferric, it will at once reverse because of the reaction $Cu^{+} + Fe^{+++} = Cu^{++} + Fe^{++}$. Furthermore, if the solution contains iron in addition to copper, another inflection point will be obtained when the ferrous ion is all oxidized (Figure 2). The finely divided sponge copper obtained reacts with surprising rapidity with the dichromate in the hydrochloric acid solution. Under these conditions there is no reaction between ferrous and cupric ions, so that a clean-cut differentiation between iron and copper can be made. Table V shows the results both with copper alone and with copper-iron mixtures.

Table V—Titration of Copper and Copper-Iron Mixtures with Potassium Dichromate after Reduction with Chromous Chloride

(Approximate initial volume, 50 cc.)

$CrCl_2$ Cc.	Concd. HCl Cc.	Cu taken Gram	Cu found Gram	Fe taken Gram	Fe found Gram
25	2	0.1075	0.1073	0	0
15	5	0.1115	0.1116	0	0
25	10	0.1256	0.1259	0	0
25	15	0.1224	0.1230	0.1099	0.1098
15	8	0.0790	0.0791	0.1153	0.1153
20	8	0.1087	0.1090	0.1073	0.1075
25	8	0.0974	0.0971	0.0996	0.0996
15	5	0.0784	0.0786	0.0832	0.0834

These results show that the amounts of iron and of copper are reproduced as well by direct potentiometric titration as by any of the standard volumetric methods now in use.

Procedure Finally Adopted—Dissolve the sample of copper ore, matte, or concentrate (0.3 to 0.4 gram according to the nature of material and the concentration of dichromate solution used for titration) in 10 cc. of aqua regia and evaporate to dryness with an excess of concentrated hydrochloric acid to convert all nitrates to chlorides. Take up with a minimum volume of water, add 1 to 2 cc. of concentrated hydrochloric acid, and digest a few minutes to redissolve any basic salts. Filter off the gangue, draining the filtrate into a 200-cc., tall electrolytic beaker. It is desirable to wash by decantation, applying four changes of minimum volumes of water. Add 5 to 10 cc. of concentrated hydrochloric acid, cover with a layer of previously purified kerosene about an inch thick, and add chromous chloride solution until the solution becomes red with suspended, finely divided copper. Add 10 to 15 cubic centimeters of the chromous chloride solution in excess, to make certain of completeness of reduction, as well as to require a sufficient amount of the dichromate so that the first inflection (Cr^{++} to Cr^{+++}) can be accurately determined. If the motor stirrer is kept running during this step, the reduction of the copper and iron is very prompt and complete. It is desirable to limit the initial volume of solution titrated to between 50 and 70 cc., as the end points are not quite so sharp at greater dilutions. Titration is then made at room temperature, with dichromate solution. Allow the dichromate to run into the unknown solution at a slow rate, and observe the behavior of the galvanometer of the titration unit. When it gives warning of the approaching inflection point, take readings at intervals of 0.1 or 0.2 cc., and find the true end point by interpolation instead of by the tedious plotting of curves. The operator can quickly develop skill in detecting the approach and arrival of the inflection point and govern the addition of reagent solution accordingly.

Table VI—Application of Chromous Chloride-Dichromate Method to Determination of Copper and Iron in a Matte

Sample Gram	Initial volume titrated Cc.	$CrCl_2$ added Cc.	Concd. HCl Cc.	Cu present Gram	Cu found Gram	Cu Per cent	Fe present Gram	Fe found Gram	Fe Per cent
0.4360	60	15	1	0.1609	0.1615	36.81	0.1465	0.1467	33.63
0.3627	60	15	5	0.1339	0.1336	36.86	0.1219	0.1223	33.70
0.3226	50	10	8	0.1190	0.1192	36.95	0.1084	0.1081	33.50
0.3138	50	10	10	0.1158	0.1155	36.80	0.1055	0.1053	33.56
0.3229	50	10	2	0.1191	0.1193	36.93	0.1085	0.1086	33.64

Mean per cent copper, 36.87 Mean per cent iron, 33.65

As far as interfering elements are concerned, magnesium, aluminium, calcium, manganese, zinc, silver, lead, sodium, and potassium would not interfere, and the titration can generally be carried out in the presence of the gangue without filtration, or in the presence of the sulfur which often separates out during dissolution of the sample. Molybdenum, selenium, arsenic, and antimony, which are sometimes present in metallurgical products, might interfere if present in considerable quantity, but could be taken care of readily—as, for instance, by boiling with granulated zinc in acid solution, thus removing the arsenic as arsine, antimony as stibine, etc. The inflections in the curves, which are as a rule strikingly sharp, reproduce the percentages of copper and iron as shown in Table VI and Figure 2.

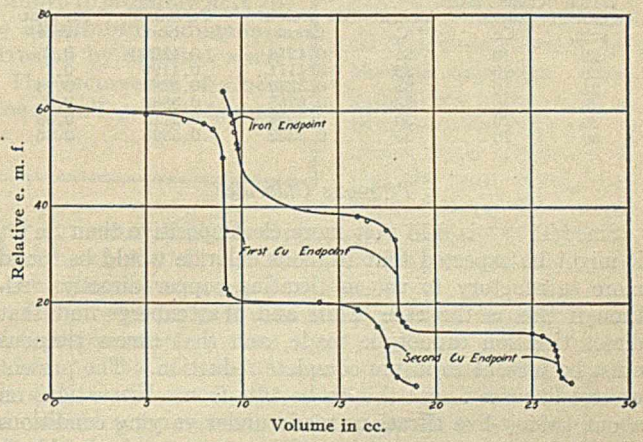


Figure 3—Direct Titration with Chromous Chloride

The samples tested were taken from a composite copper matte prepared under direction of P. P. Butler, superintendent of the Copper Queen Reduction Works of the Phelps-Dodge Corporation at Douglas, Ariz., and had been sent out by him to nineteen smelter chemists of the state to be analyzed for copper, iron, sulfur, etc., so that a comparison of precision of various laboratories as well as of different methods of analysis might be made. He found as a general average of the results the following: copper, 36.89 ± 0.1 per cent; iron, 33.60 ± 0.1 per cent. The results in Table VI are in sufficient agreement to guarantee the reliability of the method. Not only is a great saving of time claimed by this simplified procedure, but also of money, yet preserving the fundamental condition of precision. It is estimated that copper and iron can be determined accurately in less than 50 per cent of the time now required, and in some cases the time has actually been reduced to 25 per cent of what it now takes to obtain accurate results for these elements in any of the metallurigcal products, such as mattes, ores, and concentrates. It has not been applied to products very low in copper, such as slags and tailings.

Direct Titration of Copper and Iron with Standard Reducing Agents

It was considered of interest to attack this problem also from the point of view of direct titration with standard solutions of reducing agents—namely, stannous chloride, titanous chloride, and chromous chloride.

Stannous Chloride

As already stated, it appears certain that copper is completely reduced (in the absence of oxygen) by stannous chloride, and the difficulties there cited—namely, that of interaction of cuprous with mercuric ion added for removal of excess stannous, and of the inability to titrate selectively the stannous and cuprous—could be overcome by titrating directly with this reagent. Tenth normal stannous chloride did not give a sufficiently sharp inflection at the end point, so it was decided to employ 0.5 *N* solution, using, of course, correspondingly larger copper samples. This change in concentration of titrating reagent, together with the condition of titrating in hot, concentrated, strongly acid solution, resulted in fair agreement in some instances, but as a rule the results were high, even under rigorous exclusion of atmospheric oxygen. The method was not applied to mixtures of copper and iron for this reason. It is to be noted, however, that reduction is complete when an excess of stannous chloride is used. Table VII gives some of the results of titration with stannous chloride solution.

Table VII—Titration of Copper with Stannous Chloride Solution

Initial volume of soln.	Concd. HCl added Cc.	Temp. ° C.	Cu present Gram	Cu found Gram	Per cent error
20	10	85	0.4278	0.4308	0.7
20	20	30	0.4171	0.4199	0.7
25	10	85	0.3280	0.3288	0.24
25	10	85	0.3255	0.3330	2.3
30	20	30	0.2098	0.2118	0.95
50	20	85	0.5392	0.5395	0.06

Titanous Chloride

Since Ti^{+++} is 0.14 volt more electropositive than Sn^{++}, it might be expected that titanous chloride would be found more satisfactory to use in titrating copper directly. Although this is the case, Zintl and Wattenberg[2] find that direct titration cannot be made, and that excess titanous must be present to insure complete reduction. The present writers likewise found this to be true from observations on about twenty-five titrations made under varying conditions of initial volume and volume of concentrated hydrochloric acid added; the results were uniformly high, varying from 1 to 6 per cent. This scheme was therefore abandoned as a possibility of determining copper and iron by direct titration.

Note—Kolthoff[5] obtains accurate results for copper and iron by employing potassium thiocyanate or potassium iodate, which are added to the solution after the iron end point is reached in the direct titration with titanous chloride. As the titration proceeds the copper precipitates out as cuprous thiocyanate. Without the use of these reagents, they too fail to obtain satisfactory results by direct titration with titanous chloride.

Chromous Chloride

From their experiments with chromous chloride, the writers believed that direct titration would be successful, and found this to be true both in the case of copper alone and in mixtures of copper and iron. The reduction of copper proceeds in steps: Cu^{++} to Cu^{+} and Cu^{+} to Cu°. If iron is present it is reduced first. In solutions of low acidity[5] these steps are realized electrometrically. Titrations were made in low concentration of hydrochloric acid, acetic acid, and in presence of excess calcium carbonate. The latter reagents removed the free acid present in the chromous chloride solution remaining from its original preparation. Typical curves are shown in Figure 3, and the results are tabulated in Table VIII. The inflection points in the curves are extraordinarily sharp and permit of an accurate determination of the end point. In most cases interpolation was employed for determining the end points, which saved much of the labor of plotting curves.

[5] Zintl, *Z. Elektrochem.*, **31**, 429 (1925). It is very probable that the reduction potential of chromous ion varies considerably with the hydrogen-ion concentration, as Zintl finds to be true of titanous chloride. *See also* Kolthoff, *Rec. trav. chim.*, **43**, 772 (1924).

Table VIII—Direct Titration of Copper and of Copper-Iron Mixtures by Standard Chromous Chloride Solution

Initial volume Cc.	Acid present	Cu taken Gram	Cu found Gram	Fe taken Gram	Fe found Gram
30	HCl from $CrCl_2$	0.0789	0.0786	0	0
		0.0789	0.0783	0	0
		0.0790	0.0789	0	0
25	HAc–NaAc	0.1122	0.1120	0	0
		0.1208	0.1206	0	0
25	$CaCO_3$ in excess	0.1100	0.1097	0	0
		0.1107	0.1107	0	0
30	HCl from $CrCl_2$	0.0655	0.0682	0.0636	0.0636
		0.0636	0.0656	0.0643	0.0632
		0.0740	0.0771	0.0632	0.0632
30	HAc–NaAc	0.1112	0.1114	0.0958	0.0958
		0.1098	0.1101	0.0967	0.0968
30	$CaCO_3$	0.1109	0.1109	0.1008	0.1007
		0.1021	0.1023	0.1005	0.1005
		0.1110	0.1114	0.1010	0.1009

From these data the writers feel justified in concluding that reduction with chromous chloride under the conditions specified is quantitative. In large volume it was impossible to secure any degree of reproducibility or agreement; in small volume, however, the end points were sharp, but not always in absolute agreement for the two stages of copper reduction, the first being somewhat higher than the second. The first involves the changes Cu^{++} to Cu^{+} and the second, Cu^{+} to Cu°, the latter of which is very easily discernible to the eye, since the red copper powder separates out. The only explanation they have found for the high result for the first copper inflection is that at this point metallic copper does not begin to separate out until all cupric ions are reduced. The equilibrium $Cu^{\circ} + Cu^{++} = 2\ Cu^{+}$ must be satisfied. Since copper does not separate out unless a slight excess of chromous ion is present, the additional amount of chromous ion so added is believed to account for the high result. The mean of the two inflection volumes for Cu^{++} to Cu^{+} and Cu^{+} to Cu° gives the true percentage of copper, and the values so obtained are given in Table VIII.

Conclusion

In commercial practice it will perhaps be desirable to make reduction with chromous ion and titrate with dichromate, since the latter can more easily be kept at constant normality and also since the chromous chloride is added in excess and its normality need never be definitely known. Inasmuch as this reagent can be so easily prepared from such ordinary reagents as potassium dichromate, arsenic-free zinc, and hydrochloric acid, it can be recommended for smelter laboratory use. The writers have tested its constancy over periods of time, in nearly neutral solution, acid solution, in the presence of rubber, etc., and find it to be a relatively stable, though powerful reducing agent.

Research on Detonating Silver Compounds—In connection with the general study intended to develop new uses for silver, research work on detonating silver compounds has been undertaken by the Bureau of Mines. The silver salts that are considered to have explosive properties have been made and tested, and their sensitiveness to heat and impact and explosive strength determined. Experimental work has been conducted with silver azide, silver fulminate, the silver salts of some of the nitroaromatic compounds, and silver oxalate. Work has been completed on silver acetylide and the silver salt of trinitrohydroxyaminobenzene. Other silver compounds were tested but did not have any of the essential properties of an explosive.

Sand-Cast Aluminium-Manganese Alloys[1]

By Samuel Daniels

War Department, Air Service, McCook Field, Dayton, Ohio

The composition and characteristics of aluminium alloys to which manganese is added are outlined. The binary sand-cast aluminium alloys are hardly to be chosen for their mechanical properties, and heat treatment does not improve them in any way. More than about 2 per cent of manganese increases the shrinkage, the unsoundness, and the difficulties in machining. On the other hand, this element does not, like most others, detract from the normal resistance of commercially pure aluminium to salt-spray corrosion, and in ternary and more complex alloys it probably acts to improve this resistance. The aluminium-manganese alloys are less resistant to corrosion by distilled water than to that by salt spray. The occurrence of a new compound, possibly MnSi, is the metallographic feature of the series.

MANGANESE occurs in metallic aluminium and its alloys both as an impurity and as an actual addition. Primary aluminium ingot as a rule does not carry more than 0.06 per cent of manganese from the reduction of the ore, and the consequences from this small amount of impurity are negligible. When, however, from 0.25 per cent upward of manganese is added in order to form binary or more complex alloys their physical and mechanical characteristics are affected quite perceptibly. Aluminium-base alloys seldom are richer in added manganese than 2 per cent, the workable materials being usually less highly manganiferous than those for casting purposes.

There are two binary compositions employed commercially in this country—the 98 aluminium–2 manganese, for small castings required to resist corrosion by salt water, weak organic acids, etc.; and the 98.5 aluminium–1.25 manganese, in the wrought condition, also for parts to be corrosion-resistant. The former has an ultimate strength of about 17,000 pounds per square inch and an elongation in 5.08 cm. (2 inches) of about 5 per cent, and the latter, depending upon the temper and gage may have an ultimate strength of from 16,000 to 45,000 pounds per square inch and an elongation in 5.08 cm. (2 inches) of from 25 to 1 per cent.

Manganese is also a prominent constituent in a number of ternary and, more important, quaternary proprietary alloys. The 97 aluminium–2 copper–1 manganese alloy is a soft, low-strength material for castings, possessing good resistance to corrosion, especially by salt water, but having the disadvantage of a low proportional limit of less than 2000 pounds per square inch. It is not suitable for castings which must be tapped for threaded parts and which are subjected to vibration. The 85 aluminium–14 copper–1 manganese alloy received some prominence in England during the war as a piston stock. The manganese was found to increase the strength at moderately elevated temperatures, and the loss in thermal conductivity it occasioned was restored by annealing at about 454° C. (850° F.). The mechanical properties of this alloy as sand-cast are approximately 22,000–1.0–75. (These figures refer to ultimate strength—elongation in 5.08 cm. (2 inches)—Brinell hardness, 10 mm. ball, 500 kg. load, applied for 30 seconds.) The wrought, Duralumin-type of alloy, with about 4 per cent of copper, 0.5 per cent each of manganese and magnesium, and sometimes with a small quantity of chromium, is a better known material. The manganese therein contributes toward prevention of cracking during rolling, to a fibrous structure, and to enhancement of resistance to corrosion. The alloy, after heat treatment, develops an ultimate strength of approximately 55,000 pounds per square inch, an elongation in 5.08 cm. (2 inches) of about 18 per cent, and a Brinell hardness of from 90 to 110. A more recent, workable alloy, which is proprietary and of properties generally similar to those of the foregoing alloy, contains about 4.5 per cent of copper, 1 per cent of silicon, and 0.75 per cent of manganese. It is said to have better fabricating properties than Duralumin and its freedom from magnesium substantially decreases its tendency to age (harden) at room temperature, which is of importance when forming operations must follow quenching. These strong, ductile alloys, with their low specific gravity, are of distinct importance from the engineering standpoint.

It has been customary not to add to aluminium-base alloys more than about 1 per cent of manganese, because of the foundry and other difficulties which this element engenders. Manganese has been known to increase shrinkage. It unites with aluminium to give the hard, brittle compound $MnAl_3$, which, forming a eutectic at about 3 per cent of manganese and at approximately 650° C. (1202° F.),[2] is of minor solubility in the aluminium-rich solid solution (Figure 1).

The present paper is one of a number of investigations of the properties of various aluminium-alloy systems undertaken by the Material Section, Engineering Division, Air Service, U. S. A. In this article are discussed the effects of additions to aluminium of manganese in quantities less than 10 per cent.

Method of Alloying

Five melts of aluminium-manganese alloys were sand-cast in the form of test specimens, to the calculated manganese contents of 0.5, 1.0, 3.0, 5.0, and 9.6 per cent, as Melts 4469, 4470, 4471, 4473, and 4474, respectively. The aluminium ingot was of "Special" grade under Air Service Specification 11,010-B and contained 99.55 per cent of aluminium, by difference, and no manganese. The manganese was introduced through a commercial aluminium-manganese hardener bearing 9.66 per cent of manganese. The exact analyses of the aluminium ingot and the hardener are given in Table I.

Table I—Percentage Composition of Raw Materials

Melt	Material	Copper	Silicon	Iron	Manganese	Aluminium (diff.)
3538	Al ingot	0.04	0.15	0.26	None	99.55
3848	Al-Mn hardener	0.82	0.37	0.57	9.66	...

Four alloys were prepared in 15-pound lots by melting the requisite amounts of ingot and of hardener together in

[1] Received September 3, 1925. Published by permission of Chief of Air Service, War Department.

[2] Hindrichs, *Z. anorg. Chem.*, **59**, 444 (1908).

a plumbago crucible. The alloy with 9.6 per cent of manganese was simply the remelted hardener. All the alloys were poured at 704° C. (1300° F.) except this last, which was cast from 871° C. (1600° F.), in view of its much higher liquidus (about 820° C., or 1508° F.). It was found that

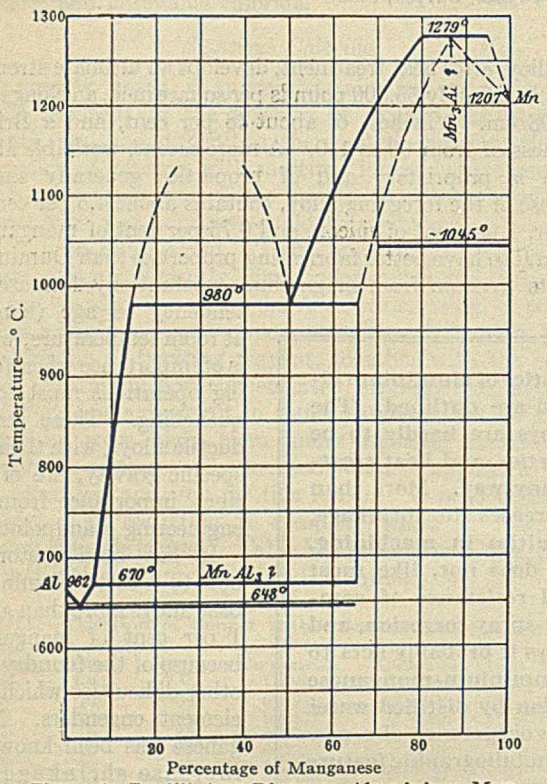


Figure 1—Equilibrium Diagram, Aluminium-Manganese System (Hindrichs)

704° C. (1300° F.) was scarcely hot enough to pour the 5.0 per cent alloy properly. The complete schedule of the foundry practice is recorded in Table II.

Table II—Foundry Practice
(Furnace, Monarch; fuel, oil; weight of charge, 15 pounds)

Melt	Time in furnace Minutes	Temperature Max. furnace ° C.	° F.	Pouring ° C.	° F.
4469	20	727	1340	702	1295
4470	20	727	1340	702	1295
4471	15	788	1450	704	1300
4473	25	771	1420	707	1305
4474	20	927	1700	871	1600

Method of Casting Test Specimens

From each melt two molds of tension test specimens were cast to size (1.28 cm. or 0.505 inch diameter), three to the mold, with individual risers and a common pouring sprue, in green sand composed of approximately equal parts of Sandusky and of Albany sand. A photograph of the Air Service standard TB-1 test bar mold has been shown in a previous article.[3] Temperature measurements were made with a bare chromel-alumel couple and a potentiometer.

Method of Testing

Chemical Analysis—The aluminium ingot and the hardener were analyzed for copper, iron, and silicon by standard methods. The manganese content was determined in all samples by the sodium arsenite method. The weights of samples for the aluminium ingot and for the 0.5, 1.0, 3.0, 5.0, and 9.6 per cent manganese alloys were, respectively, 0.1, 0.1, 0.1, 0.3, 0.2, and 0.2 gram. The last three solutions were diluted to 500, 500, and 1000 cc., respectively, and the analysis was made on 50 cc. Using the entire solution, the manganese content of the hardener was checked by the bismuthate method (0.25-gram sample) to within 0.06 per cent. The results of these determinations are indicated in Tables I and III.

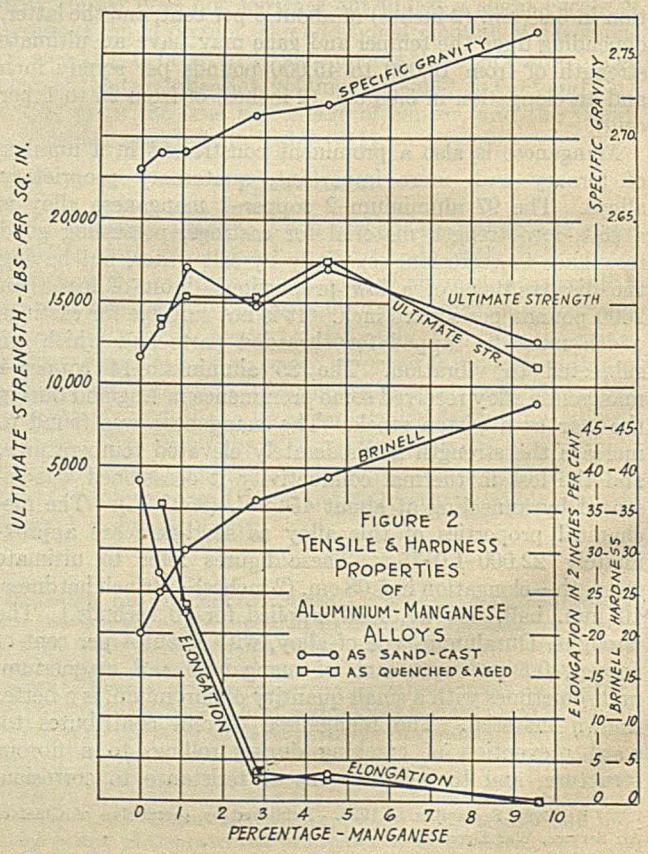
Table III—Chemical Analysis and Mechanical Properties of Al-Mn Alloys

Melt	Manganese Per cent	Ultimate strength Lb./sq. in.	Elongation in 5.08 cm. (2 in.) Per cent	Brinell hardness	Specific gravity
		As sand-cast			
3538	None	11,750	38.5	20	2.68
4469	0.54	13,930	27.2	25	2.691
4470	1.02	17,030	22.6	30	2.696
4471	2.88	14,900	2.6	36	2.713
4473	4.56	16,860	3.0	39	2.720
4474	9.60	12,560	None	48	2.765
		As quenched and aged (1025-96CW 300-2)			
4469	0.54	13,960	35.8	24	2.690
4470	1.02	15,430	23.3	27	2.697
4471	2.88	15,300	3.3	35	2.715
4473	4.56	16,930	2.3	40	2.723
4474	9.60	11,300	None	48	2.769

Mechanical Testing—Tensile, Brinell hardness (500 kg. load, 10 mm. ball, 30 seconds), and specific gravity tests were made according to standard methods and with the results embodied in Table III and in Figure 2. Each value is the average taken from three bars in similar condition of treatment, with the exception that only one specific gravity test was made to represent each mold of specimens. The as-cast bars were tested 11 days after casting, and the heat-treated 3 days after the completion of heat treatment.

Corrosion Testing—The unmachined grip ends of broken specimens both as cast and as heat-treated were subjected to corrosion tests in distilled water and in salt spray. For the purpose of comparison there were included in the tests a sample of the aluminium (permanent-mold) ingot from which the aluminium-manganese series was prepared and unmachined grip ends from test bars in the 92 aluminium–8 copper alloy.

In the distilled-water test each manganese alloy was represented in a 400-cc. beaker by two grip-end specimens—one



[3] Daniels, This Journal, 16, 1243 (1924).

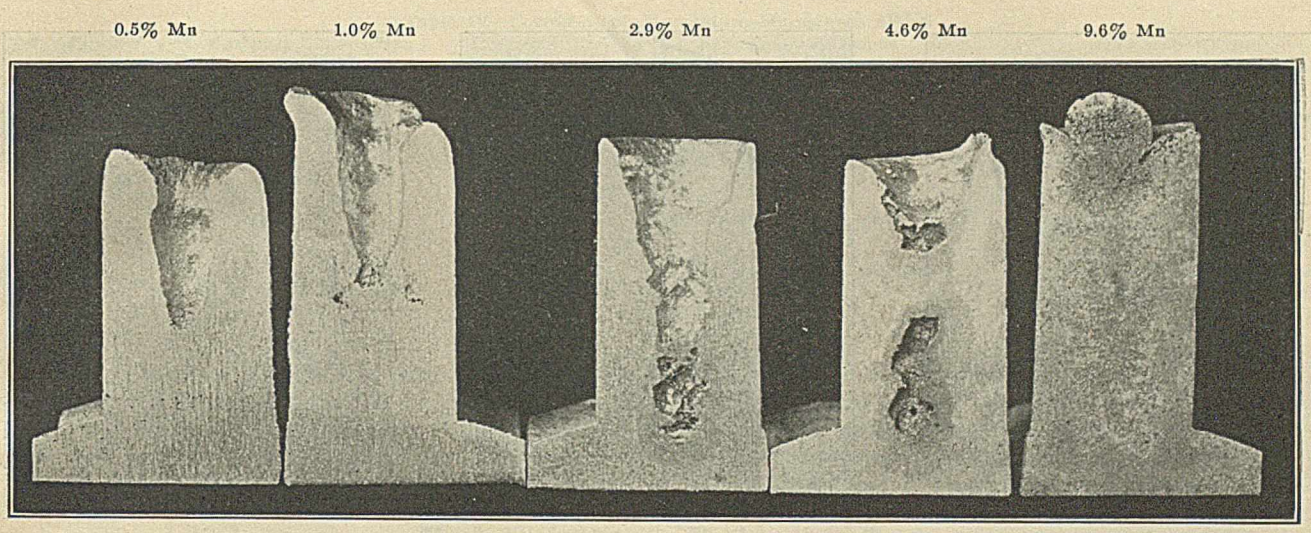


Figure 3—Shrinkage (Pouring-Sprue) of Aluminium-Manganese Alloys, with Increasing Manganese Content to Right

as cast, the other as heat-treated. These were then immersed in sufficient water to cover 5 cm. (2 inches) of the specimen and to permit also a study of the water-line corrosion. The same treatment was simultaneously accorded unmachined specimens from the aluminium ingot and from the 8 per cent copper alloy. The exposure consumed 30 days.

The salt spray test involved placing a similar set of specimens on glass supports in an inclosure continually permeated with the indirect spray from an atomized 20 per cent salt solution. The humidity was practically 100 per cent at all times. The spray period was 100 hours.

Method of Heat Treatment

In order to ascertain whether quenching and aging would improve the mechanical properties of the alloys through the possible solution and reprecipitation of soluble compounds, one mold of each analysis was soaked for 96 hours at 580° C. (1075° F.), about 52° C. (125° F.) below the eutectic temperature, in an electric furnace automatically controlled to within ± 5.5° C. (10° F.). The bars were then quenched into cold water and thereafter aged in an electric oven at 149° C. (300° F.) for 2 hours.

Preparation and Examination of Metallographic Specimens

A 1.27-cm. (0.5-inch) transverse metallographic specimen was cut from the riser end of the middle bar in each cast and in each heat-treated mold. The procedure for polishing the specimens has been outlined in a previous article.[3] They were examined, unetched and etched, at low, at intermediate, and at high (1.9 mm. objective under oil immersion) magnification.

A study of the constituents unetched revealed that silicon, of slaty tinge, is easily recognizable, but that the watery blue $MnAl_3$ is difficult to distinguish from iron-bearing constituents, from the blue-gray skeletons, filigree, and fringes of another constituent of intimate association, which are thought, at least in part, to be manganese silicide (MnSi, or perhaps MnAlSi), and, to less degree, from the cores of pinkish Mn_3Al(?), occurring in the 9.6 per cent manganese alloy. The MnSi, however, appears to be harder than the $MnAl_3$ on relief-polishing, which stains the former a light brown. This type of polishing also lessens the natural color-contrast between MnSi and the cores; but the fact still remains that the silicide takes the characteristic forms of filigree, fringes, or detached skeletons, whereas the cores are always sheathed with $MnAl_3$. As to the iron-bearing constituents, it is believed that purple $FeAl_3$ skeletons are present in all the alloys but that they are hardly to be distinguished from the MnSi and $MnAl_3$. In several cases needles of $FeAl_3$ were indentified on the bases of form and of color.

Among the etching reagents tried were a 1 per cent aqueous solution of sodium hydroxide, with (Lantsberry) and without 2 per cent of hydrogen peroxide, cold and boiling distilled water, an acid ferric chloride reagent, 5 per cent aqueous sodium hydroxide, and 2 per cent aqueous hydrofluoric acid. The 1 per cent caustic solutions bring out latent scratches and stain the $MnAl_3$ and Mn_3Al irregularly, without altering the color of the silicide, which is sharply outlined. In short etching periods $MnAl_3$ turns light brown, while the cores are watery blue. The coloration becomes variegated with protracted immersion. The acid ferric chloride solution blackens the silicide. Cold and boiling distilled water cause pitting and nonuniform staining of the manganese aluminides. A dip in 5 per cent aqueous sodium hydroxide until hydrogen is evolved turns $MnAl_3$ brown and leaves the cores difficultly distinguishable in color, at least, from the silicide, which is not attacked. Longer immersions sharpen the boundaries of the compounds and make the $MnAl_3$ blue to black and the cores brown. The shorter etch is preferable. Etching in 2 per cent aqueous hydrofluoric acid until hydrogen is evolved sharply outlines all the constituents, especially the MnSi, which, while the other compounds are not affected, is stained brown. This etch is preferred to longer immersions, which blacken the silicide. The 5 per cent sodium hydroxide and the 2 per cent hydrofluoric acid etchants, used in conjunction with one another, are quite helpful.

Foundry, Machining, and Mechanical Properties

Cast Alloys—The addition of much more than about 1 per cent of manganese results in foundry and other difficulties. This element increases the shrinkage (Figure 3) and promotes porosity when present in appreciable quantity. Such unsoundness was especially observable in the metallographic sections. In the 9.6 per cent manganese alloy the internal stresses were of sufficient magnitude to cause an exudation of liquid eutectic. A lathe test to compare the machinability of the 4.6 per cent manganese alloy with that of the 8 per cent copper alloy showed that the latter gave a longer chip, was more free-cutting, and took a much smoother finish. The former material machined like cast iron. The hard, brittle compound $MnAl_3$, which seems to drag and drop out, is probably responsible for this action.

Figure 4—0.5 Mn. × 100
Sand cast. 13,930–27.2–25. $MnAl_3$ and iron-bearing skeletons

Figure 5—0.5 Mn. × 500
Sand-cast. $MnAl_3$ skeletons

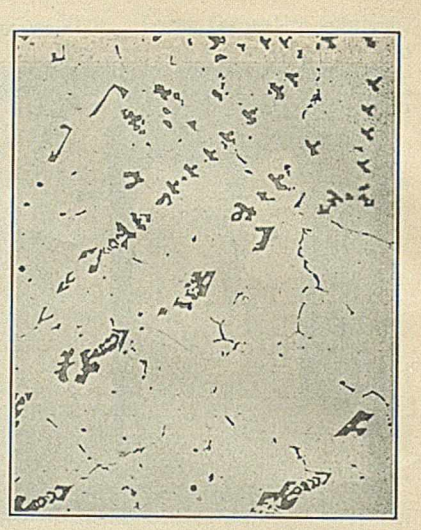


Figure 6—2.9 Mn. × 100
Sand-cast. 14,900–2.6–36. Disjointed spines of $MnAl_3$ (larger particles) and filmy iron-bearing skeletons

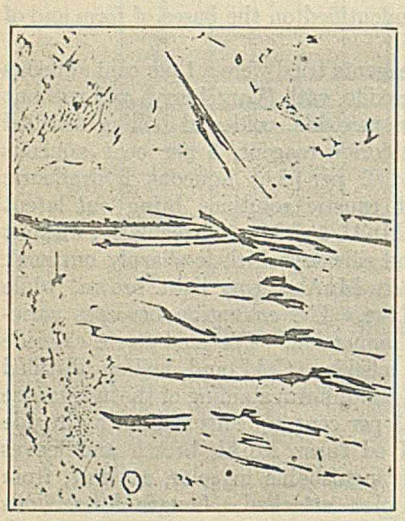


Figure 7—2.9 Mn. × 100
Quenched and aged. 15,300–3.3–35. Needle formation of primary and fine eutectic areas of $MnAl_3$

Figure 8—4.6 Mn. × 100
Sand-cast. 16,860–3.0–39. Rhomboidal $MnAl_3$, characteristic for this content of manganese

Figure 9—9.6 Mn. × 100
Sand-cast. 12,560–0–48. Duplex needles containing $MnAl_3$ sheathes and Mn_2Al cores

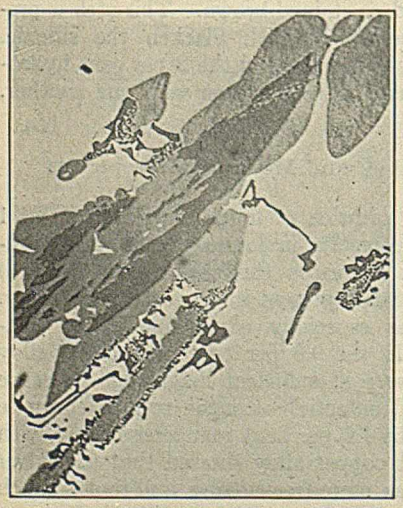


Figure 10—9.6 Mn. × 500
Sand-cast. $MnAl_3$ (light), Mn_2Al cores (half-tone), and MnSi (?) fringes

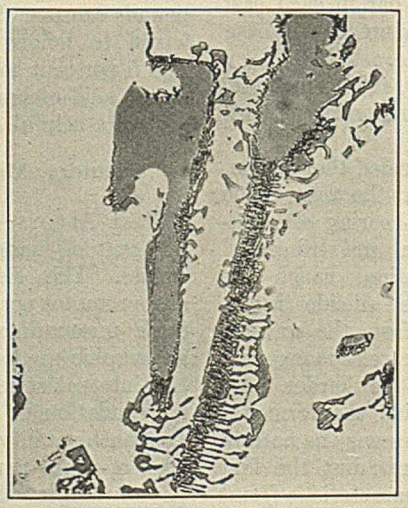


Figure 11—9.6 Mn. × 500
Sand-cast. $MnAl_3$ (gray) and fringes of MnSi (?) evidently formed from $MnAl_3$

Figure 12—9.6 Mn. × 100
Quenched and aged. 11,300–0–48. Manganiferous ($MnAl_3$) needles, from which cores have been almost entirely removed by heat treatment

Table IV—Corrosion of Aluminium-Manganese Alloys

Specimen	Chemical Composition	Condition	Salt Spray Exposure	Distilled Water
4470–1	1.0 Mn-Al	As cast	Trace of corrosion on all manganese alloys in 24 hours. Heat treatment does not improve corrosion resistance. Very little corrosion in 100 hours. All manganese alloys affected similarly in regard to the extent of corrosion	Manganese alloys show brown corrosion spots. Very slight on all specimens in 48 hours. Corrode slightly less than the 8 per cent copper alloys in one month
4470–2		As heat-treated		
4471–1	2.9 Mn-Al	As cast		
4471–2		As heat-treated		
4473–1	4.6 Mn-Al	As cast		
4473–2		As heat-treated		
4474–1[a]	9.6 Mn-Al	As cast		
4474–2		As heat-treated		
4539–2	8.0 Cu-Al	As cast	Corroded in less than 5 hours	Corrosion perceptible in less than 24 hours
3538 Ingot	Cu 0.04, Si 0.14, Fe 0.26, Al balance	As received	Corroded similar to manganese alloys	One month in distilled water caused more corrosion than 100 hours in salt spray

[a] Remelt of Melt 3848.

As far as ultimate strength and percentage of elongation are concerned, there is not much to be gained for the sand-cast alloys by introducing much more than, perhaps, 2 per cent of manganese (Table III and Figure 2). In fact, the binary alloys of aluminium with manganese are hardly to be chosen for their strength, for 20,000 pounds per square inch would probably be a maximum. The decline in elongation which occurred for the alloys containing 1.0 and 2.9 per cent of manganese is so abrupt that the curve would have been strengthened had a 2 per cent alloy been included in the series. The Brinell hardness graph manifests a gradual increase with manganese content from 20 to 48. In this respect its trend is dissimilar to that of ultimate strength, which begins to fall away after about 5 per cent of manganese is passed. It is thought, however, that too much reliance cannot be placed upon the strength and the elongation curve for the alloys higher in manganese, as they appear sensitive to pouring temperature. The specific gravity rises regularly with the percentage of manganese.

Figure 13—9.6 Mn. × 500
Quenched and aged. Cores nearly removed by heat treatment. Compare with Figure 10

Heat-Treated Alloys—Hardly any difference was found physically or mechanically between the cast and the heat-treated test specimens (Table III and Figure 2).

Corrosion

In the distilled-water test the corrosion products of the manganese alloys varied in color from a mixture of brown and white on the low-manganese alloys to solid brown on the high-manganese alloys. This brown deposit is evidently manganic hydroxide.[4] The extent of corrosion of the manganese alloys was about the same as that of the pure aluminium, but slightly less than that of the 8 per cent copper alloy. Neither increase in manganese content over 1 per cent nor heat treatment altered the behavior of the several alloys.

It seems peculiar that these tests showed that the aluminium-manganese alloys are rather readily attacked by distilled water but are more corrosion-resistant to salt spray (Table IV). After 100 hours in the spray they and the aluminium ingot showed only slight corrosion, which was white in color and probably aluminium hydroxide. Analysis of the corrosion product on the 9.6 per cent manganese alloy gave 4.5 per cent of manganese, which indicates that the solution of manganese from its hard compounds is quite slow. The 1 per cent alloy, however, was practically as resistant as the alloys richer in manganese, and heat treatment did not affect the corrodibility. All these alloys were superior in this respect to the 8 per cent copper alloy and compared favorably with the aluminium-silicon alloys.

[4] Institute Mechanical Engineers, Ninth Report to the Alloys Research Committee, 1910, p. 283.

Metallography

The addition of 0.54 per cent of manganese caused in the as-cast alloy the appearance of $MnAl_3$ chiefly as skeletons (Figures 4 and 5), but also as needles and small rounded particles. Iron-bearing needles and skeletons were also evidently present, though not easily differentiated, because of meager size, from the ordinarily lighter-colored $MnAl_3$. With this latter constituent were often associated tiny blue-gray colonies of what may be MnSi. The heat treatment of this alloy produced no structural change except the appearance of a slight intragranular precipitate of $MnAl_3$ (Figure 14).

As the manganese content is increased the skeletons of $MnAl_3$ became larger and more ramified and the needles stouter until, with about the eutectic ratio, the rhomboidal habit began to crop out and the columnar arrangement was common (Figure 6). Primary $MnAl_3$ was found in the segregated areas, close by more characteristically eutectic $MnAl_3$ (Figure 7). The nature and amount of the constituents other than and except $MnAl_3$ did not change perceptibly. With 4.6 per cent of manganese primary, rhomboidal $MnAl_3$ was abundant (Figure 8). After the heat treatment of these alloys the intragranular precipitate or coagulate of $MnAl_3$ was apparent—the only noticeable structural change.

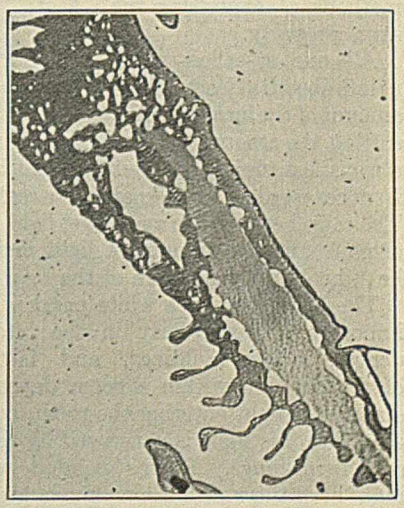


Figure 14—9.6 Mn. × 1000
$MnAl_3$ surrounded by MnSi (?) fringes. Note intragranular precipitate of $MnAl_3$

As cast, the 9.6 per cent manganese alloy had cores of M_3Al(?) sheathed with $MnAl_3$ (Figures 9 and 10). The evidence for the occurrence of the MnSi constituent is pre-

sented in Figure 11. The watery blue particles of $MnAl_3$ have evidently reacted with the liquid to form another blue-gray enfringing constituent. Massive chunks of purple $FeAl_3$ were found associated with Mn_3Al, but this type of $FeAl_3$ was absent in the other alloys, in which the iron content was considerably lower. Heat treatment removed the cores nearly in entirety (compare Figures 12 and 13 with Figures 9 and 10). Figure 14 is of $MnAl_3$, the MnSi(?) fringe, and the abundant intragranular precipitate of $MnAl_3$.

Acknowledgment

Grateful acknowledgment is herewith made to A. C. Zimmerman, Clifford McMahon, and to John L. Hester for their assistance in this experimentation.

Factors Determining the Brightness and Opacity of White Paints[1]

By F. H. Rhodes and J. S. Fonda

Cornell University, Ithaca, N. Y.

A formula is developed to express the relation between the brightness of a film of white paint and the thickness of the film, and experimental evidence in support of this formula is advanced. The well-known effect of the addition of a small amount of black pigment in increasing the hiding power of a white paint is explained. Attention is called to the possible effect of the roughness of the surface of a paint film upon the brightness of the film.

THE opacity of a paint may be defined as the ability of the paint to obstruct the transmission of visible light. This property is of very great importance to the user, since upon the opacity depend the quantity and the number of coats of paint required to obscure the surface over which the paint is applied. To obtain complete hiding with a paint of low opacity a large quantity of paint and a large number of coats will be required, so that both the cost of material and the cost of application will be high. By some authorities a distinction has been drawn between opacity or degree of obstruction to visible light, and hiding power or ability to obscure the underlying surface. This distinction is not a valid one; the two terms are simply two methods of expressing the same property.

All our so-called white paints absorb at least a small amount of the incident light, so that the amount of light reflected by the painted surface is always less than the amount of light incident to that surface. In other words, "white" paints are really gray instead of white. The ratio between the amount of light reflected by a given film of paint and the amount of light incident to that film may be taken as the measure of the brightness of the film.

The brightness of a white paint is of very great practical importance, particularly in the interior painting of residences, office buildings, and factories. The intensity of illumination within a room depends not only upon the amount of light entering the room, but also upon the extent to which this light is conserved by reflection from the walls and furnishings. Rooms painted with a white paint of high brightness will show much greater average intensity of illumination with the same input of light than will rooms painted with a paint of low reflecting power. Moreover, the use of a paint of high reflecting power facilitates uniform illumination and minimizes the variation in the intensity of light caused by the irregular distribution of light sources.

It is apparent that when a so-called white paint is applied over a black surface the brightness of the painted surface will depend to large extent upon the opacity and thickness of the film. With very thin films or relatively transparent paints a considerable amount of the incident light will be transmitted to the underlying dark surface and will there be absorbed, so that the brightness will be low. As the thickness of the film of white paint is increased by increasing either the number of coats or the thickness of the individual coats, less and less light is transmitted and the brightness of the painted surface increases, until finally a point is reached at which practically all of the incident light is either reflected or absorbed by the paint film itself. When this point is reached further increase in the thickness of the film produces no measurable increase in brightness. The brightness of such an opaque film of any particular paint may be termed the "ultimate brightness" of that paint.

It is obvious that the thickness of the film of any particular paint which is required to attain the ultimate brightness for that paint will decrease as the opacity of the film increases. The actual brightness of any thin film of a paint is a function of both the ultimate brightness and the opacity. The opacity of a film of paint is, in turn, dependent on the thickness of the film, the ratio of the refractive index of the pigment to the refractive index of the vehicle, the volume percentage of pigment in the paint, the average size (diameter) of the pigment particles, and the shape and structure of the individual particles of pigment.

The substances that are used as paint pigments are, in massive form, transparent. The whiteness of the white pigments in their usual finely divided condition is due to the multiple reflection and refraction of the incident light at the very large number of exposed surfaces. Since the amount of reflection that takes place in a light ray that passes at a given angle from one transparent medium into another increases with the difference between the refractive indices of the two media, it is apparent that the total amount of reflection from a finely divided pigment suspended in a transparent vehicle will increase with the difference between the refractive index of the pigment and that of the vehicle. Since the suspending medium in an ordinary paint is oxidized linseed oil, the opacity of a paint should increase as the difference between the refractive index of the pigment and that of the oxidized oil.

This fact has been recognized by most investigators in this field. Several investigators have determined the brightness and opacity of dry paint pigments or of suspensions of pigments in water and glycerol, and have proceeded to use

[1] Received June 1, 1925.

the data thus obtained as a basis for the comparison of the brightness and opacities of paints prepared from these pigments. In this previous work the tacit assumption has been made that the relation between the opacities of suspensions of any two pigments depends primarily upon the refractive indices of the two pigments alone and is substantially independent of the refractive indices of the suspending media. This assumption is not justified. Even the relative order of the opacities of a series of pigments may be different when the pigments are suspended in media of different refractive indices. Some work has been done upon the opacity of suspensions of pigments in unoxidized (liquid) linseed oil. Results thus obtained can probably be applied with a fair degree of accuracy to the comparison of the opacities of dried paint films from these pigments, although some slight error may be introduced because of the change in the refractive index of the vehicle during drying. In determining the opacities of various substances when used as paint pigment the most logical procedure is, however, to measure directly the opacities of dry films of actual paints prepared from these pigments.

In comparing the hiding power and opacities of various pigments, many investigators have taken a unit weight of pigment as the basis of comparison. With paints made from pigments of the same refractive index and particle size the hiding power should vary with the percentage by volume of pigment in the paint. For this reason it is more logical to take a unit volume of pigment as the basis in comparing the opacities of different pigments. This fact has been generally, but not universally, recognized by investigators in this field.

Since the brightness and opacity of a film of white paint are due to the multiple reflection and refraction of the light at the interfaces between oil and pigment, it is obvious that opacity and brightness should increase as the number of such interfaces in the film increases—i. e., as the average diameter of the pigment particles decreases. The shape and the interior structure of the pigment particles themselves may also have some effect upon the hiding power of the paint. Pigments composed of particles that are irregular in shape and possess interior fracture should show higher opacity than pigments of which the particles are smooth and perfect.

Previous Methods

Various methods have been used to determine the brightness and opacity of paints. A procedure[2] in common use is to rub down a standard quantity of white pigment with a standard amount of linseed oil and ultramarine blue and to note the tint of the resulting paint. When two white pigments are thus tested, the one giving the lighter paint is said to have the higher hiding power.[3] A modification of this method, using carbon black instead of ultramarine blue, has been used by Hallett.[4] This method, however, does not necessarily give a quantitatively correct measure of the opacity or the brightness of the white paint pigment.

Wolff[5] measured the opacity of a paint by measuring the exact thickness of a film of the liquid paint which was required to obscure completely a black surface covered by the paint. This method is subject to three possible criticisms:

1—Measurements were made with liquid paints rather than with dry paint films.

2—Data thus obtained apply only to thickness of film required to give complete hiding and give no information as to the nature of the variation of opacity with film thickness.

3—Since the paints are used in the liquid form, any specific effect of the nature of the surface of the dry paint film upon the hiding power and brightness is neglected.

Pfund[3] has described an instrument which he terms a "cryptometer" and which is used to measure accurately the exact thickness of wet paint required to obscure completely a black surface. Measurements made by this cryptometer are subject to the same criticisms as those made by Wolff.

In a subsequent article Pfund[6] gives some data as to the comparative brightness and opacity of a number of pigments, and discusses the effects of the addition of small amounts of black pigment upon these characteristics of a white paint. He found that, in general, the addition of black pigment sufficient to increase the hiding power 5 per cent decreased the brightness only 1 per cent.

Other methods have been used to some extent. G. W. Thompson[7] described an instrument called an "opacimeter." With this apparatus he measured the opacities of paints in the liquid form by measuring the light transmitted through various thicknesses of paint. Sheppard[8] used a turbidimeter, which determined how well a liquid paint will hide a grating submerged in it.

Hallett[9] points out that measurements of the hiding power of paints should be made on the dry paint film rather than on the liquid paint. By means of a special instrument devised by him and termed a "hidimeter," he measured the comparative hiding powers of a series of white paint pigments.

In a subsequent article Hallett[4] developed the following mathematical formula for correlating the hiding power of a film of paint, the hiding power of a unit thickness of film, and the thickness of the film expressed in terms of such unit thicknesses:

$$a = 1-\sqrt[n]{1-S}$$

where a = hiding power of unit thickness
n = number of unit thicknesses in film
S = hiding power of film expressed as fraction of complete hiding

He found that the hiding powers of the dry paint films as measured by his hidimeter agree closely with the hiding powers as predicted from cryptometer readings made with the wet paint, and showed that the hiding power and the tinting power of the pigments measured bore a direct linear relationship to each other. In his work Hallett was concerned primarily with the hiding power of the paint and made no direct measurements of the ultimate brightnesses of the paints when applied in films thick enough to give complete hiding.

Gardner[10] has made some measurements of the whiteness of suspensions of pigments in nitrocellulose solution and in varnish, but the results are not, of course, quantitatively applicable to ordinary paints.

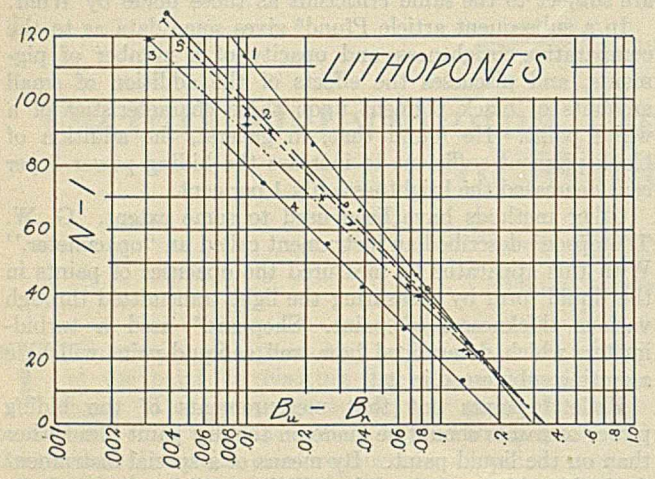
Experimental

In the present investigation an attempt was made to determine the hiding powers and whitenesses of films of various white paints and to define the relationship of the hiding power to the thickness of film, refractive index of the pigment, particle size of the pigment, and volume percentage of pigment in the paint. Paints were prepared from a series of white pigments of known refractive index and measured particle size. From these paints films of known thickness and known volume percentage of pigment were applied and the whiteness and hiding power of each such film were meas-

[2] Calbeck, *Proc. Am. Soc. Testing Materials*, **22**, 515 (1922).
[3] Pfund, *J. Franklin Inst.*, **188**, 675 (1919).
[4] *Proc. Am. Soc. Testing Materials*, **22**, II, 523 (1922).
[5] *Farben-Ztg.*, **16**, 2577 (1910); through *Chem. Zentr.*, **82**, II, 809 (1911).
[6] *J. Franklin Inst.*, **196**, 69 (1923).
[7] Paper presented before the American Institute of Chemical Engineers, December, 1912.
[8] This Journal, **12**, 167 (1920).
[9] *Proc. Am. Soc. Testing Materials*, **20**, II, 426 (1920).
[10] *Paint Mfrs.' Assoc. U. S., Circular* **133** (September, 1921).

ured. A mathematical formula was developed to express the correlation of hiding power with its various determining factors and was found to apply with reasonable accuracy in all the paints which were studied.

The paints used were prepared from pigment, pure refined linseed oil, and drier, and were thinned to the proper working consistency with pure gum turpentine.



The linseed oil used was pure refined oil from North American seed, showing the following analysis:

Refractive index	1.4790
Specific gravity	0.933
Saponification number	192.5
Iodine number	181.1
Acid value	0.5645

The drier used was lead-manganese linoleate dissolved in turpentine. This drier solution contained 1.16 per cent lead and 0.347 per cent manganese.

In preparing the paints the following standard formula was adopted, which gave paints of fairly satisfactory consistency with almost all of the pigments used:

	Grams
Pigment	67
Oil	33
Turpentine	8
Drier solution	1.8

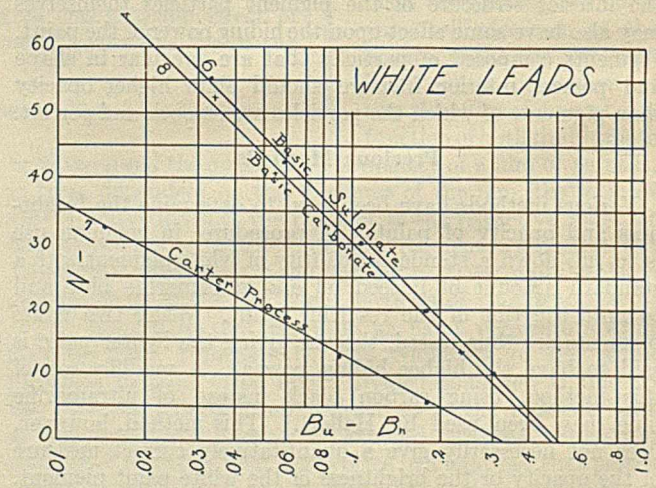
The paints were applied to panels of white pine, 10 × 61 cm. (4 × 24 inches), which had been prepared as follows: The panels were first given a coat of flat black paint and allowed to dry. A coat of shellac was then applied in order to fill any pores of the wood and to prevent the flat black from staining any subsequent coats of white paint. The dry, shellaced surface was rubbed down lightly with very fine sandpaper to dull the gloss and to provide a slightly roughened surface to which the subsequent coat of paint would adhere. In applying the white paint to the pan a beaker containing a portion of the paint, together with the brush with which it was to be applied, was weighed accurately. A coat of uniform and proper thickness was applied so as to cover a 51-cm. (20-inch) length the full width of the panel, leaving a 10-cm. (4-inch) square at one end unpainted. The beaker, brush, and unused paint were then weighed. After this first coat was thoroughly dry a similar coat was applied to a 41-cm. (16-inch) length of the panel thus leaving a 10-cm. (4-inch) square covered with but one coat of the white paint. Successive coats were similarly applied, thus leaving a series of squares covered with 0, 1, 2, 3, 4, and 5 coats of white paint, respectively. In the case of some paints the hiding power of the first coat was so low as to be practically nil, so the second coat was applied over the same area as the first. This procedure was found necessary in the case of two of the paints made from barytes and gave, therefore, a series of squares on the panel covered with 0, 2, 3, 4, 5, and 6 coats, respectively.

After the last coat of paint had thoroughly dried, measurements of the whiteness of each of the painted areas were made. The instrument used was an integrating photometer similar to that described by Taylor.[11] This instrument has been shown to give true readings of the ratio of the amount of reflected light to the amount of incident light and therefore may be used for the direct determination of the whiteness of a painted surface.

The average diameter of particle for each pigment was determined by the method described by Green.[12] In most cases the writers' results agree fairly well with those obtained by Green for similar pigments, most of the variations being not greater than the differences in fineness which might exist among various samples of the same pigment. The pigment which the writers have termed simply "basic carbonate white lead," and which was supplied as a representative sample of white lead made by the Dutch process, was, however, very much finer and more uniform in size than true Dutch process white lead, and was probably a precipitated basic carbonate. Since the discrepancy was not discovered until after the measurements of the whiteness and hiding power had been made, the data for this pigment are included, although they should be understood not to be typical of true Dutch process white lead.

Calculations

Knowing the exact weight of paint applied, in each coat, per unit of surface, and the exact percentage by weight of pigment in each paint, it was possible to calculate the exact weight of pigment in each coat or series of coats on each unit area. From the density of the individul pigments as obtained from published tables,[13] the volume of pigment per unit area



and the depth of pigment, considered as a solid layer, was calculated. From this result and the data as to the average particle diameter of the pigment, it is possible to calculate the number of superimposed unit layers of particles of pigment in any given coat, or series of coats of any particular paint could be determined. The formula for calculating the number of superimposed particles of pigment in any given film was:

[11] *Bur. Standards, Sci. Paper* **405**.

[12] "A Photomicrographic Method for the Determination of Particle Size of Paint and Rubber Pigments," Research Bulletin issued by New Jersey Zinc Company.

[13] *U. S. Geol. Survey, Bull.* **679**.

$$n = K \frac{10{,}000\ GP}{Atd}$$

where n = number of superimposed unit layers of particles
G = weight (grams) of paint applied to any known area
A = area (sq. cm.) covered by G grams of paint
P = fraction, by weight, of pigment in paint
d = density of pigment
t = average diameter of pigment particles, in microns, or 10,000 times the average diameter in cm.
K = constant depending on the shape of the pigment particles and on their arrangement in the film

Since the value of K cannot be determined accurately for any individual paint, the value of one was arbitrarily assigned to this constant. The effect of the error thus introduced will be discussed later.

When a ray of light falls on a film of white paint, a certain portion is reflected from the upper surface of the film while the remainder enters the body of the film. The amount of light reflected at the upper surface of the paint will depend largely upon the roughness of the surface and upon the refractive index of the vehicle, and will be practically independent of the nature of the pigment except as this may effect the roughness of the surface of the film. Thus, if from the same pigment two paints are prepared, one of which dries to a "flat" surface and the other to a glossy surface, thin films of the flat paint will show greater whiteness than will similar films of the glossy paint. In the same way a plate of ground glass shows greater whiteness than a smooth glass plate, although the refractive index of the material is the same in both cases.

Of the light which actually enters the film a portion is reflected at the interfaces between pigment and vehicle and is thus returned as reflected light, a portion is transmitted to the under surface, and a portion is absorbed in the film itself. Of that light which is transmitted through the film a portion may be reflected at the under surface and reappear as reflected light. In the writers' work, however, the amount of light obtained by reflection from the black under surface was so small that it was neglected.

It should be possible to develop a mathematical formula which will correlate the hiding power and whiteness of a film of any particular paint and the thickness of that film expressed in terms of the average diameter of the pigment particles. Such a formula may be developed as follows:

Let a = the fraction of the incident light which actually enters the film
$1-a$ = the fraction of the incident light which is reflected from the upper surface of the film
n = the number of unit layers of pigment particles in the film
R = portion of light incident to any one unit layer of pigment particles which is directly reflected upward to next upper layer
A = portion of light incident to any one unit layer of pigment particles which is directly absorbed within that layer
T = portion of light incident to any one unit layer of pigment particles which is directly transmitted through that layer
U = amount of light reflected by any one unit layer and passing upward out of film
B = brightness
B_r = brightness due to reflected light passing upward from *within* the film
B_n = brightness of any film of n unit layers of pigment particles
B_u = ultimate brightness—i. e., brightness of a film of paint so thick as to be opaque

By definition

$$T = 1-A-R \text{ and} \qquad (1)$$

$$B_r = (U_1 + U_2 - - - + U_n) \qquad (2)$$

The amount of light reflected by the upper layer of pigment particles, U_1, is equal to R. The amount of light transmitted by the upper layer of particles is T.

Of the light reaching the second layer of particles, T, a portion, RT, is reflected by this second layer. Of this reflected light, one part, ART, is absorbed by the upper layer, a second part, RRT, is re-reflected downward by the first layer, and a third part, $RT\text{-}ART\text{-}RRT$, or RT^2, emerges from the paint film. Of the light re-reflected downward by the first layer of particles, R^2T, a portion, R^3T, is again reflected upward by the second layer and R^3T^2 emerges from the film. Thus, the total light reflected by the second layer of particles and reappearing as emergent light is

$$\begin{aligned} & RT^2 + R^3T^2 + R^5T^2 - - - + R^\alpha T^2 \\ &= RT^2 (1 + R^2 + R^4 - - - R^\alpha) \\ &= RT^2S, \text{ where } S = (1 + R^2 + R^4 - - + R^\alpha) \end{aligned}$$

In a similar manner the total light emerging from the film after reflection from the third unit layer of pigment particles is

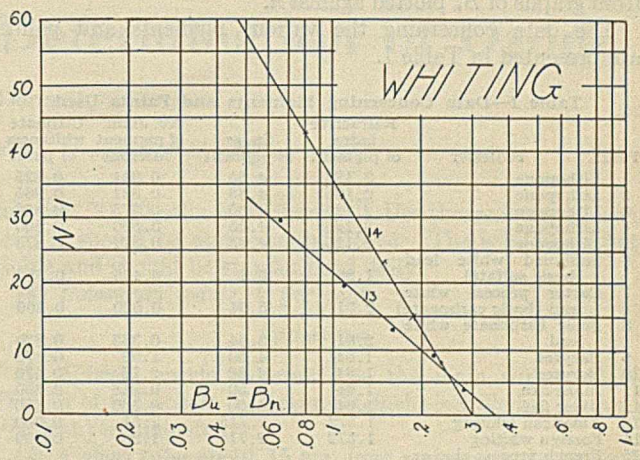
$$U_3 = RT^4S^3$$

and

$$U_n = RT^2S\,(T^2S^2)^{(n-2)} \quad \text{or}$$
$$= RT^2SM^{(n-2)}$$

where

$$M = T^2S^2 \qquad (3)$$



Thus far it has been tacitly assumed that all the incident light actually enters the film. As a matter of fact, some of the light, $1-a$, is reflected at the interface between the paint and the air, and only a portion, a, really enters the film. Thus we have

$$\begin{aligned} B_n &= (1-a) + aR + aRT^2S + aRT^2SM - - - - + aRT^2SM^{(n-2)} \qquad (4) \\ &= (1-a) + aR + aRT^2S\,(1 + M - - M^{(n-2)}) \\ &= (1-a) + aR + aRT^2S \left[\frac{1-M^{(n-1)}}{1-M}\right] \qquad (5) \end{aligned}$$

From this we derive the equation

$$\frac{(1-m)\,(1-a+aR)}{aRT^2S} - \frac{(1-M)B_n}{aRT^2S} = M^{(n-1)}$$

or

$$K_1 - K_2B_n = M^{(n-1)} \qquad (6)$$

From (3),

$$M = T^2S^2$$

where

$$S = (1 + R^2 + R^4 - - - R^\alpha) = \frac{1}{1-R^2}$$

The maximum value of R is $(1-T)$, so that for the maximum value of R,

$$S = \frac{1}{1-(1-T)^2} = \frac{1}{2T-T^2}$$

The corresponding value of M is $\left(\frac{1}{2-T}\right)^2$. The minimum value of R is 0, in which case M becomes equal to T^2. Since T is always less than 1, $M^{(n-1)}$ approaches 0 as n is increased. Thus we have

$$K_1 - K_2B_u = 0 \qquad (7)$$

Similarly, when n=1, $M^{(n-1)}=1$ and

$$K_1-K_2B_1 = 1 \qquad (8)$$

From these equations we can evaluate the constants K_1 and K_2 in terms of B_u (the ultimate brightness) and B_1 (the brightness of a film consisting of a single layer of pigment particles). We thus obtain the values:

$$K_1 = \frac{B_u}{B_u-B_1}, \text{ and } K_2 = \frac{1}{B_u-B_1}$$

Substituting these in Equation 6 we have

$$\frac{B_u}{B_u-B_1} - \frac{B_n}{B_u-B_1} = M^{(n-1)}$$

or

$$B_u-B_n = (B_u-B_1)\ M^{(n-1)} \qquad (9)$$

or $\log (B_u-B_n) = \log (B_u-B_1) + (n-1) \log M$

$$\log (B_u-B_n) = K + (n-1) \log M \qquad (10)$$

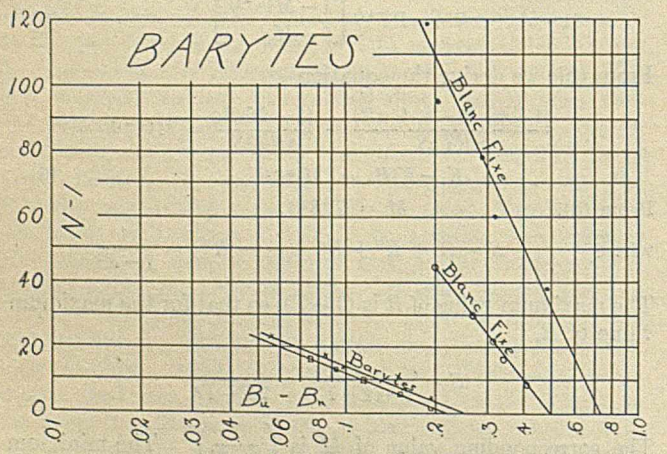
Obviously, therefore, when the logarithms of B_u-B_n are plotted against the corresponding values of $(n-1)$ a straight line should result. The values of B_n are obtained by direct measurement, while values of B_u are gotten by extrapolation from graphs of B_n plotted against n.

The data concerning the various pigments and paints are presented in Table I.

Table I—Data Concerning Pigments and Paints Used

Paint	Pigment	Refractive index of pigment	Sp. gr. of pigment	Av. diam. of pigment Microns	Ultimate whiteness of paint
1	Lithopone	2.125	4.35	0.341	0.825
2	Lithopone	2.125	4.35	0.331	0.935
3	Lithopone	2.125	4.35	0.375	0.873
4	Lithopone	2.125	4.35	0.520	0.860
5	Lithopone	2.125	4.35	0.371	0.875
6	Sublimed white lead (basic sulfate)	1.88	6.4	0.435	0.883
7	Carter process white lead (basic carbonate)	2.01	6.64	0.620	0.860
8	Basic carbonate white lead	2.01	6.64	0.385	0.860
9	Barytes	1.64	4.50	1.99	0.470
10	Barytes	1.64	4.50	2.77	0.470
11	Blanc fixe	1.64	4.50	0.948	0.800
12	Blanc fixe	1.64	4.50	0.460	0.800
13	American whiting	1.572	2.715	2.51	0.600
14	Foreign whiting	1.572	2.715	1.96	0.600
15	French process zinc oxide	2.02	5.23	0.350	0.902
16	"U. S. P." zinc oxide	2.02	5.23	0.500	0.892
17	"Lehigh" American process zinc oxide	2.02	5.45	0.500	0.873

For each of these paints the values of B_u-B_n are plotted against the corresponding values of $n-1$, using arithmetical-logarithmic paper and plotting the values of B_u-B_n on the logarithmic scale. It will be observed that in almost every case the points fall on or close to a straight line, thus

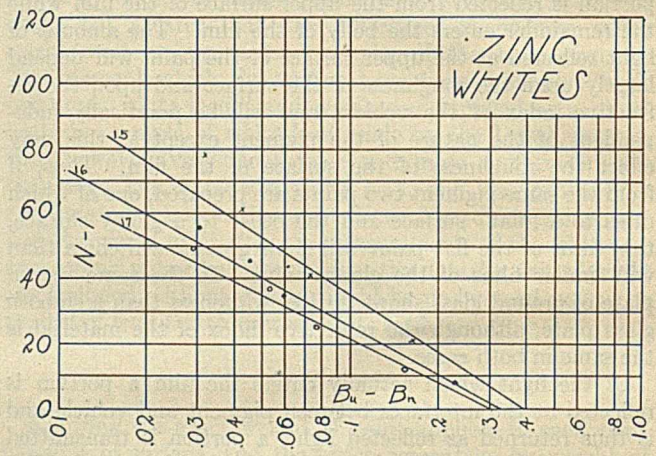


demonstrating the correctness of the formula given above. The least consistent results were obtained in the case of the zinc oxide pigments. The authors are inclined to attribute the somewhat erratic results obtained with this pigment to the tendency of the particles of zinc oxide to agglomerate. In plotting the results obtained with the zinc oxide pigments the greatest weight is given to the data obtained with the thinner films, since the probable error in determining B_u-B_n increases rapidly as B_n approaches B_u.

As has been stated above, the values of n are calculated from the formula

$$n = K\,\frac{10{,}000\ GP}{Atd}$$

in which the constant K has been assigned the arbitrary value of 1. The effect of using this admittedly incorrect arbitrary value instead of the unknown true value is simply to multiply n by a constant factor and thus to change the slope of the graph but not its essential form.



From the graphs of B_u-B_n plotted against $n-1$ the comparative hiding powers of the various white paint pigments can be computed. According to Konig and Brodhun, the least difference in brightness that is perceptible to the human eye is from 1 to 2 per cent. It follows, therefore, that complete hiding is secured when B_u-B_n becomes approximately equal to 0.02. If the number of unit layers (of any given pigment) required to give a value of 0.02 for B_u-B_n be multiplied by the average diameter of the particles of that pigment, the results should be proportional to the volume of that pigment required to give apparently complete hiding. The reciprocals of these values will be proportional to the hiding powers of the various pigments, expresssd in terms of volume. In Table II the hiding power of lithopone is assigned the arbitrary value of 80 and the values for the other pigments are calculated from their ratios to this arbitrary standard. Corresponding values obtained by Hallett are given for comparison.

Table II—Relative Hiding Power per Unit Volume of Pigment

Pigment	Rhodes and Fonda	Hallett
Lithopone	80	80
Basic lead sulfate	86	72
Carbonate white lead	99	100
Blanc fixe	16.4	
Whiting	15 to 20	
Zinc oxide	90	96

Since the two sets of measurements were made by different methods, with samples of pigment which probably differed somewhat in particle size and other properties, the results are reasonably consistent. It should be noted that in calculating back to thickness in terms of unit volume of pigment any error due to arbitrary assumptions as to the arrangement of the particles is eliminated.

The value of B_1 for each paint represents the portion of the total incident light which would be reflected by a film of paint containing a single layer of pigment particles when illuminated by parallel light striking the surface at the

particular angle of incidence adopted in the photometer used. Obviously, B_1 is equal to the sum of the light reflected at the interface between the air and the film of oil above the first layer of pigment particles and the light reflected at the interface between the pigment particles and the film of oil above them. The writers' data do not afford sufficient basis for the separate evaluation of these factors. It is possible that the light reflected at the interface between the air and the paint film is a very considerable portion of the total light reflected by the film. If so, the brightness of a film of white paint should depend, in part, upon the viscosity and the surface tension of the vehicle, extent to which the vehicle shrinks during drying, and other factors which affect the smoothness of the surface of the film. The study of the effects of these factors on brightness offers an interesting field for further study.

A number of investigators have found that when a small amount of dark pigment, such as carbon black or Prussian blue, is added to a white paint the increase in the hiding power of the paint is very much more pronounced than is the decrease in brightness. The authors have not seen any adequate explanation of this phenomenon. It may be explained as follows:

From Equation 9 we have

$$B_u - B_n = (B_u - B_1)\, M^{(n-1)}$$

where

$$M = T^2S^2$$

$$\text{or } B_u - B_n = (B_u - B_1)\,(T^2S^2)^{(n-1)}$$

If a dark pigment is added to the paint, T will be decreased and $(T^2S^2)^{(n-1)}$ will be decreased very greatly. For any given thickness of film the value of $B_u - B_n$ will be very much less than before, and the point at which the differences between B_u and B_n ceases to be visible will be reached with a much thinner film than before the dark pigment was added. In other words, the addition of the dark pigment should very greatly increase the hiding power of the paint.

A Quick Method for the Determination of Ozone[1]

By H. B. McDonnell

Agricultural Experiment Station, University of Maryland, College Park, Md.

THIS method is used in checking the operation of an ozonizer at the University of Maryland Agricultural Experiment Station. As ordinarily geared this machine delivers approximately 2800 liters (100 cubic feet) of ozonized air per minute at 9 cm. of water pressure. The method is a modification of one used by Todd,[2] which is, briefly, as follows: From a nozzle with an outlet 1.5 mm. ($^1/_{16}$ inch) in diameter the ozonized air is allowed to flow for 15 seconds through a glass tube dipping 2.5 cm. (1 inch) into 30 cc. of a 1 per cent potassium iodide solution containing starch. The color obtained is compared with that from an equal volume of solution containing 5 cc. of a 0.01 per cent iodine solution to which is added starch solution.

Instead of comparing the blue solutions the writer found it more convenient to add to the testing solution of potassium iodide and starch an amount of sodium thiosulfate solution equivalent to 5 cc. of the 0.01 per cent iodine solution and pass the ozonized air through until the blue color appeared, noting the time with a stopwatch. The amount of ozone varies inversely with the time.

Under the conditions of the test it was found that approximately 790 cc. of ozonized air passed through the test solution in 15 seconds, which would indicate approximately 90 parts of ozone per million by weight, which was the concentration desired.

Solutions

(1) *Starch.* Mix 2 grams of soluble starch with about 5 cc. of cold water and add 100 cc. boiling water. This should be kept cool and renewed after 2 to 4 days.

(2) *Iodine,* 0.01 per cent. Dissolve 0.1 gram iodine in about 10 cc. water, with the aid of about 2 grams potassium iodide, and make up to 1 liter. This solution is fairly stable for 1 or 2 months if kept in the dark.

(3) *Sodium thiosulfate,* approximately equivalent to solution (2). Test by taking 5 cc. of (2) in a flask, add the same amount of water and 3 or 4 drops of (1). From a buret add solution (3) till color is discharged. Use this amount in each test; it should be approximately 5 cc. The solution is not stable and should be standardized daily.

(4) *Potassium iodide,* 1 per cent.

Apparatus

(1) A brass nozzle to screw into the main supply pipe. The tip of the nozzle for 6 mm. ($^1/_4$ inch) is drilled to 1.5 mm. ($^1/_{16}$ inch) in diameter.

(2) A glass tube about 15 cm. long and 4 mm. bore, bent about 45 degrees 3 cm. from one end, the other end ground off at an angle so that the flow of gas will not be obstructed when the end of the tube rests against the bottom of the test bottle. This tube is attached to the nozzle by a short piece of rubber tubing.

(3) Test bottle. A 60-cc., wide-mouth packing bottle, which 30 cc. should fill to a height of 2.5 cm., where it should be marked with a file.

Test

To the test bottle add the proper amount of the standard thiosulfate solution; fill to the mark with potassium iodide solution and add 4 or 5 drops of starch solution. Attach the glass tube to the brass nozzle, bring the test bottle over the end of the glass tube till the end of the tube touches the bottom of bottle, and note time for the appearance of blue color by use of a stopwatch. The concentration of ozone is inversely proportional to the time.

The method is applicable to low concentrations where the amount of ozone used in the test is not over 1 mg. For higher concentrations the potassium hydroxide liberated causes low results. (The reviewer suggests the addition of a little boric acid to the thiosulfate and potassium iodide solution to adapt the method to higher concentrations.) The pressure and standards are arbitrary and may be varied to meet individual conditions.

This method can also be used for dilute mixtures of chlorine and air.

[1] Presented before the Division of Water Sewage and Sanitation at the 69th Meeting of the American Chemical Society, Baltimore, Md., April 6 to 10, 1925.

[2] "Experiments with Oxygen on Disease."

Note—Riesenfeld and Bencker [*Z. anorg. Chem.*, **98**, 167 (1916)] have also reported work on the action of ozone on inorganic iodine compounds.

Ultrafiltration of Vegetable Tanning Solutions[1,2]

By Arthur W. Thomas and Margaret W. Kelly

COLUMBIA UNIVERSITY, NEW YORK, N. Y.

THE process of ultrafiltration popularized by the ingenuity of Bechhold[3] is generally accepted as a means of separating colloids from crystalloids. This is based upon the fact that colloidal particles are large compared with crystalloidal particles. The separation of such particles by the ultrafiltration membrane is quite generally, though incorrectly, accepted to be entirely mechanical in nature—i. e., that the membrane acts merely like a sieve.

Sheppard,[4] in a study of the nature of solution of certain dyes as revealed by their absorption spectra, found that when absorbed in collodion films they gave the colors and absorption spectra of true solutions of the dyes. This shows that these dyes were truly dissolved in the nitrocellulose. Some of them went into true solution in the membrane even from a state of colloidal suspension in water.

The chemical point of view regarding separation by semipermeable membranes was proposed as early as 1854 by L'Hermite,[5] who produced some interesting experiments to support his contention. He showed that ether passes through a membrane of water into chloroform. If water is placed over a layer of chloroform and ether superimposed upon the water, the chloroform layer increases in volume while the ether layer diminishes. He also impregnated a porous jar with castor oil, placed water in it, and immersed it in alcohol. The alcohol endosmosed through the castor oil membrane into the water. The passage of the ether in the first case and of the alcohol in the second instance is certainly not mechanical. While collodion membranes were not existent in 1854, animal gut was, and L'Hermite pointed out that the diffusion of water or aqueous solutes through animal membranes was identical to the endosmosis through liquids by virtue of the imbibitional faculty for water possessed by such septa.

While much of the permeability phenomena of membranes, so beautifully demonstrated by Wm. Brown,[6] might be taken to indicate a mechanical nature, yet there is experimental evidence in his work pointing conclusively to a chemical relationship between the particles passing through the membrane and the membrane substance. The dialysis of an aqueous solution of a mixture of two colloids, night blue and starch, may be cited as an example. A collodion membrane of high degree of permeability allowed starch to diffuse through, holding night blue back, whereas a formalized gelatin membrane of high degree of permeability was permeable to night blue but impervious to starch.

Ultrafiltration has recently been employed by R. Jay Browne[7] for the purpose of separating the tannins from the nontans in complex natural vegetable tannin solutions, the separation being based upon the hypothesis that ultrafiltration is a purely mechanical process, as the following quotation from his paper will show:

> There are many methods of separating the tannins from associated nontannins, but they are all tedious, and it is doubtful how far any of them yields a pure tannin. During the process, the tannin may be decomposed or otherwise changed, and it is never certain that the product obtained is the same as the tannin in the original substance. This possibility is avoided in ultrafiltration, which is purely mechanical, a mere filtration through a more resistant filter, accelerated by the application of pressure.

R. J. Browne separated gallic acid from gallotannin by ultrafiltration. Two substances of such widely differing molecular weight may be quite well separated by ultrafiltration when a suitable membrane is used. But it is quite a different matter when one attempts to separate a series of complex organic bodies, called tannins, of perhaps widely differing molecular weights and states of aggregation, from a series of organic bodies of lower yet also of widely differing molecular weights and chemical nature. Furthermore, the degrees of aggregation of all these tanning and nontanning organic bodies change markedly with the hydrogen-ion concentration of the solution. A clear gambier, hemlock, or quebracho extract at pH = 7 becomes more colloidal upon acidification, as evidenced by increase in turbidity finally resulting in precipitation when pH = 2 is reached.[8]

The tannins are weakly acidic substances of high and of as yet unknown molecular weight. Some of the known nontannins are also weakly acidic in nature. It seems almost unnecessary to point out that such bodies are readily dissolved by alkaline solutions and progressively forced out of solution by increase in hydrogen-ion concentration.

The question concerning just where the line of demarcation between the colloid (tannin) and crystalloid (nontannin) components of complicated vegetable tannin extracts shall be drawn seems hopeless, since the distinction between colloids and crystalloids is only relative, and especially futile in the case of tannins, when one considers the change in their degrees of aggregation as a function of the acidity or alkalinity of their solutions.

Another variable to be considered is the membrane used. Membranes vary over enormous ranges of permeability according to their chemical nature and mode of preparation. Wm. Brown prepared collodion membranes permeable to sodium chloride while impermeable to sodium sulfate, pervious to potassium permanganate while impervious to potassium oxalate, porous to starch yet impenetrable to Congo red and night blue. Wm. Brown was concerned only with the preparation of simple membranes, such as collodion and gelatin. He experienced difficulty in duplicating membranes of a given permeability. He was obliged to follow rigidly a definitely uniform technic in the flowing of the membrane solution, in the draining of the same and the vapor pressure of ether and alcohol during the draining, in the time of exposure to air, the temperature, the soaking in water, and in the subsequent variation of permeability by use of suitable swelling solutions.

R. J. Browne makes his membranes by immersing disks of filter paper in collodion solutions containing 6 per cent pyroxylin dissolved in alcohol and ether. This strength was adopted by him after extensive experimentation showed that membranes made with it divided a tanning extract

[1] Presented by Miss Kelly before the Division of Leather and Gelatin Chemistry at the 68th Meeting of the American Chemical Society, Ithaca, N. Y., September 8 to 13, 1924. Received October 16, 1925.

[2] Contribution No. 496 from the Department of Chemistry, Columbia University.

[3] *Z. physik. Chem.*, **60**, 257 (1907); **64**, 328 (1908); *Biochem. Z.*, **6**, 379 (1908); *Kolloid-Z.*, **2**, 3 (1907).

[4] *Proc. Roy. Soc. (London)*, **82A**, 256 (1909).

[5] *Compt. rend.*, **39**, 1177 (1854).

[6] *Biochem. J.*, **9**, 591 (1915); **11**, 40 (1917).

[7] *J. Soc. Leather Trades Chem.*, **7**, 365 (1923); *J. Am. Leather Chem. Assoc.*, **18**, 409 (1923).

[8] Thomas and Foster, THIS JOURNAL, **15**, 707 (1923).

solution into the same tannin and nontannin fractions as the official method of tannin analysis does.

In view of the rigid technic proved to be necessary by Wm. Brown (and recently verified by Eggerth[9] and by Nelson and Morgan[10]) it is interesting to note that used by R. J. Browne. Wm. Brown knew from the experience of others that the amount of alcohol and ether left in the membrane before plunging it into water controlled the degree

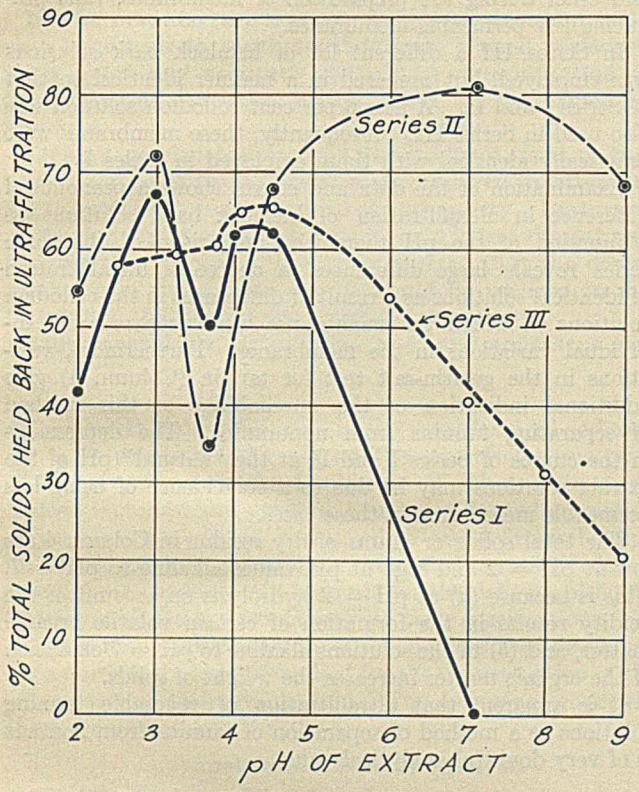


Figure 1—Ultrafiltration of Hemlock Bark

of permeability. He found it hopelessly impossible to establish a given permeability by allowing alcohol and ether to evaporate to different extents before plunging the membrane under water owing to the lack of a quick (or even slow) quantitative indicator of the extent of evaporation. He therefore dried out the organic liquids completely from the prepared membrane and subsequently brought them to varying and definitely reproducible degrees of permeability by soaking in suitable swelling baths prior to washing in water. The method of preparation of membranes used by R. J. Browne is, however, as follows:

Ordinary filter papers are soaked in the collodion solution until the evolution of air bubbles ceases. They are then drained for a few seconds, and moved horizontally in their own plane, to obtain an even surface of collodion, and after a minute or two, when the membranes become "tacky," they are immersed in water. The ether-alcohol is replaced by the water, which fixes the permeability of the membrane. The membranes are now washed in running water until free from ether-alcohol, and stored in water until ready for use. They will keep indefinitely if chloroform or toluene is added to the water to prevent the formation of mold.* * The permeability of these membranes depends very largely on the extent of drying which they undergo in the air before immersion in water, and if allowed to dry completely, they become hard and brittle, and practically impermeable. After a certain amount of practice, membranes could be prepared of desired uniformity, and differing very little in their permeability. Moreover, in some cases, it was found very useful to be able to increase the impermeability of a membrane, made from the same strength of collodion solution, by merely allowing it to dry in the air for a longer period before immersing it in water. If the membrane became too brittle by this treatment, its flexibility could be restored by soaking it in alcohol, when it would become softer and more permeable.

The method of establishing the permeability of R. J. Browne's membrane is, it is seen, to allow the ether-alcohol solvent to evaporate until the coating is "tacky," which required a minute or two. If they are not sufficiently "tacky" they will be too permeable, probably allowing tannins to pass through, while if too "tacky" they will be too impermeable, perhaps holding some nontannins back. It would appear that the method of preparing membranes was really to make a series and test them against vegetable tannin solutions, the proper ones being those which separated the components of the extract into tannin and nontannin fractions just as the official method of analysis does. Having prepared such membranes Browne has described a very good quantitative method of expressing the permeability as a function of the velocity of filtration of water under increasing pressure. The criticism raised, however, is against the procedure adopted for the determination of proper drying time—i. e., to the proper "tackiness."

Experimental

The purpose of this investigation was to show the variation in ultrafiltration of a vegetable tanning extract with change in pH value of its solution. This point was not considered by Browne, who used the extracts at the pH as he found them—i. e., at the "natural" pH.

Membranes were prepared using the same trade-marked collodion and as closely as possible according to Browne's technic, and used in the ultrafiltration of solutions of hemlock bark extract. The collodion solution was kept in a desiccator, in order to prevent loss of solvent by evaporation.

A stock solution of hemlock bark extract was prepared to contain about 1.6 grams tannin (tannin as defined by the official method of analysis). This stock solution, after adjusting to various pH values by electrometric titration with sodium hydroxide or hydrochloric acid, was diluted so as to contain 0.4 gram tannin per 100 cc. and then ultrafiltered.

The two ultrafilters used were the Columbia type. One was developed in this laboratory. The other was an improved type made by Hayes and Whitmore, of Urbana, Ill. (Figure 2) The pressure was furnished by a tank of compressed nitrogen

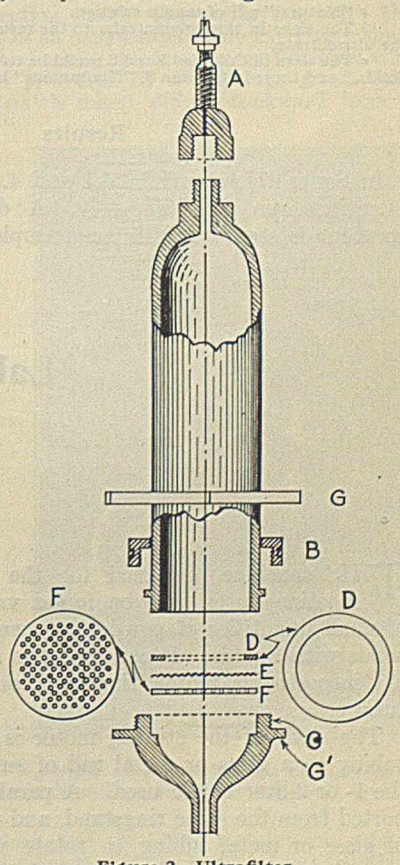


Figure 2—Ultrafilter

A = automobile tire valve
B = collar which takes up on funnel at *C*
D = rubber gasket
E = wire gauze on which membrane rests
F = perforated plate
G, *G*[1] = hexagonal form to hold in vise

[9] *J. Biol. Chem.*, **48**, 203 (1921).
[10] *Ibid.*, **58**, 305 (1923).

attached to the ultrafilter through a Hoke pressure reduction valve. Nitrogen gas was used instead of compressed air in order to avoid oxidation of the tannin solutions. The total solids of each solution, before ultrafiltration, were determined by evaporation of a definite volume of sample in the usual way, and the amount of solute passing through the ultrafilter was similarly determined by evaporation of a measured portion of the ultrafiltrate to dryness. All weights in the table refer to 25 cc. of solution.

Table I—Ultrafiltration of Hemlock Bark Tanning Solutions of Different pH Values

pH (1)	Dry residue in 25 cc. of original soln. Gram (2)	Ultrafiltrate[c] Gram (3)	Tannin test[b] (4)	Solids held back in ultrafilter[c] Gram (5)	Per cent of total solids held back[c] (6)
Series I, Pressure = 80 lbs./sq. in. (234 kg./sq. cm.)					
2.0	0.125	0.073	−	0.052	42
3.0	0.132	0.044	−	0.089	67
3.7[a]	0.130	0.065	+	0.065	50
4.0	0.131	0.050	++	0.081	62
4.5	0.131	0.050	++	0.081	62
7.1	0.135	0.135	++	0.000	0
9.0	0.140	0.141	++	0.000	0
Series II, Pressure = 200 lbs./sq. in. (586 kg./sq. cm.)					
2.0	0.122	0.055	−	0.067	55
3.0	0.131	0.037	−	0.095	72
3.7[a]	0.132	0.086	+	0.046	35
4.5	0.133	0.043	−	0.090	68
7.1	0.131	0.025	−	0.106	81
9.0	0.138	0.040	−	0.094	68
Series III, Pressure = 120 lbs./sq. in. (352 kg./sq. cm.)					
2.5	0.130	0.055	+	0.075	58
3.3	0.134	0.055	+	0.079	59
3.8[a]	0.132	0.052	+	0.080	61
4.1	0.132	0.049	+	0.083 }	64
4.1	0.132	0.045	−	0.087 }	
4.5	0.132	0.044	−	0.088 }	65
4.5	0.132	0.048	−	0.084 }	
6.0	0.137	0.064	−	0.074	54
7.0	0.138	0.082	+	0.056	41
8.0	0.140	0.097	++	0.044	31
9.0	0.148	0.118	++	0.030	20

[a] "Natural" pH of tannin solution.
[b] The signs in this column refer to the result of a gelatin-salt test upon the ultrafiltrate.
[c] The data in Columns 5 and 6 would be termed "Tannins and Insoluble Solids," and those in Column 3, "Nontannins" by Browne.

Results

In Series III, at pH = 4.1 and 4.5, are given duplicate filtrations run simultaneously. A deviation of 8 to 10 per cent is seen. This is an example of deviations due to the difference in permeability of two membranes as a result of the uncertain technic of drying to a certain "tackiness."

Series I and II were made with the same hemlock bark solutions, but the membranes used in Series II were made after a number of others had been prepared from the same 6 per cent collodion solution. This solution, although carefully protected from evaporation, had become concentrated owing to unavoidable slight evaporation of alcohol and ether during the preparation of membranes, thus producing less permeable membranes.

In Series III a different lot of hemlock bark solutions was employed, but prepared in a manner identical to that of Series I and II. A new 6 per cent collodion solution was also used in Series III; consequently, these membranes were practically identical with those employed in Series I.

Examination of the data and curves shows a pronounced difference in ultrafiltration of hemlock bark solutions as a function of the pH thereof. Comparison of the three series reveals large differences in degree of ultrafiltration of identical solutions as a result of differences in the collodion solutions in which the membranes were prepared and individual variations in the membranes. Furthermore, variations in the gelatin-salt test for tannin (Column 4) give additional indication of the unreliability of this method of separating tannins from nontannins. The depressions in the curves of Series I and II at the "natural" pH of the extract solutions may be due to a coincidence of using less permeable membranes in these cases.

The total solids or grams of dry residue in Column 4 are low at pH = 2 and high at pH values alkaline to pH = 7. This is because (*a*) at pH = 2 hydrolysis on account of the acidity results in the formation of certain volatile organic matter, and (*b*) in the solutions alkaline to pH = 7 oxidation of the organic matter increases the weight of solids.

It is apparent that ultrafiltration of vegetable tanning solutions as a method of separation of tannins from nontans is of very doubtful analytical value.

Acknowledgment

The authors are indebted to A. F. Gallun & Sons Company for grants in aid of this investigation.

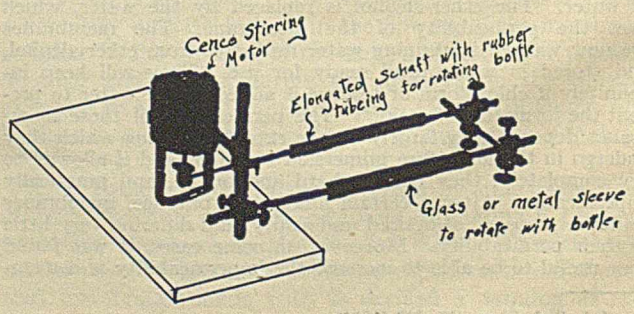
Laboratory Mixing Machine for Solids[1]

By R. M. Hixon

Iowa State College, Ames, Ia.

THIS machine, designed for the laboratory testing of nicotine dusts, will be found valuable for the mixing of small quantities of powders or even for the agitation of solids with liquids. It can be made in a few minutes with a Cenco stirring motor, ringstand, and metal rods or glass tubing.

The shaft of the stirring motor is connected by suction tubing to a glass or metal rod of sufficient length to take the 1- or 2-liter bottle used. A parallel rod is rigidly supported from the same ringstand, and provided with a sleeve of glass or metal tubing to rotate with the bottle. The outer end of the rigid rod and the elongated shaft of the motor are connected by a short rod held by Universal clamps. The driving shaft is covered with rubber tubing to give sufficient traction for rotating the bottle. Mixing paddles may be inserted in the bottle if desired.



Laboratory Mixing Machine for Solids

[1] Received December 16, 1925.

Determination of Strength of Liquid Hydrocyanic Acid by Specific Gravity[1]

By Mark Walker and C. J. Marvin

THE PACIFIC R & H CHEMICAL CORP., EL MONTE, CALIF.

In the manufacture and use of liquid hydrocyanic acid on a large scale in southern California a need developed for a quick and accurate method for determination of the purity of the acid, which could be performed in the field.

Liebig's gravimetric method did not lend itself to this work because of the difficulties encountered in attempting to analyze hydrocyanic acid of high purity. Inasmuch as the density of pure hydrocyanic acid is less than three-fourths that of water, it was recognized that the determination of the specific gravity could be utilized in determining the percentage purity of the liquid.

This paper deals with the methods and apparatus employed for preparing the set of specific gravity tables of liquid hydrocyanic acid which are appended. From these tables, given the specific gravity and temperature of the liquid, the percentage of purity can be readily determined. The method and tables are only adapted to solutions of high concentration.

After long and continued use of these tables the specific gravity determination of liquid hydrocyanic acid of relatively high purity can be said to be accurate to within ± 0.1 per cent. With the limitations necessarily imposed, the tables can be recommended for quickly and accurately determining the percentage composition of commercial liquid hydrocyanic acid.

LIQUID hydrocyanic acid is now manufactured and used in southern California for the control of citrus pests as well as for the fumigation of ships, grain warehouses, factories, and dwelling houses for the extermination of vermin. This liquid is shipped in metal drums holding up to 100 pounds net weight. Manufacturers are held responsible to the State of California for the delivery of liquid hydrocyanic acid in accordance with their specifications.

In the manufacture and use of this liquid a need developed for a quick and accurate method for the determination of the percentage of hydrocyanic acid. The following work was therefore undertaken.

Gravimetric Methods of Analysis

The fundamental principles underlying the gravimetric analysis of hydrocyanic acid offer nothing new, since the work consists merely in absorbing a known weight of liquid hydrocyanic acid in a caustic soda solution, thus forming a sodium cyanide solution which is titrated with standard silver nitrate solution using potassium iodide indicator, according to the MacArthur modification of Liebig's method.[2]

Simple as this process appears, there are several inherent difficulties which are not apparent to the novice. In the first place, since in many cases a product of high purity is to be analyzed, it is necessary to weigh accurately the sample taken. Pure hydrocyanic acid boils at 26.5° C., and since during the summer months in California the temperature is normally at or above this point during the working hours, the loss of the more volatile and pure portion of the sample is not only possible but highly probable unless special precautions are taken, thus very seriously affecting the accuracy of the work.

In gravimetric analyses of liquid hydrocyanic acid of high concentration, it has been found that the procedure of determining the specific gravity of the liquid and then measuring the volume taken for analysis is not sufficiently accurate; therefore, it is necessary to actually weigh the portion used in the determination. On account of the vapor pressure of the material, an ordinary weighing bottle is not satisfactory for this purpose, and even a specially constructed weighing tube with glass stopcocks on each end has proved inadequate to hold the fluid without loss during the weighing operation, owing to the low viscosity of the liquid and the difficulty of keeping the stopcocks sufficiently tight. The apparatus shown in Figure 1 was therefore devised to obviate the difficulties mentioned.

APPARATUS—The essential parts of this apparatus are the sampling bulb and the absorption flask. The former is fitted with two 3-way stopcocks, one of which communicates with the air and is protected by a soda-lime guard tube, while the other communicates directly with the 500-cc. sample bottle and also with the 200-cc. absorption flask. The connection with the latter is made by means of an intermediate bulb carrying a short stem on the upper end and a long slender stem on the lower end. The absorption flask is protected by a soda-lime guard tube against any moisture which might diffuse backward from a filter pump to which it is attached. The glass cylinder under one outlet from the upper stopcock catches the overflow. The hydrometer and thermometer in the cylinder are not essential to this part of the work.

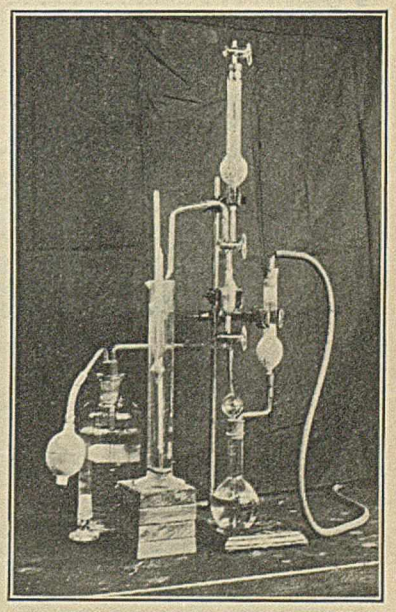


Figure 1—Apparatus for Gravimetric Determination of Hydrocyanic Acid

ABSORPTION OF HYDROCYANIC ACID—Ninety cubic centimeters of 25 per cent caustic soda solution are placed in the absorption flask. The stopper carrying the bulb is inserted and the flask and contents are weighed on an analytical balance. The flask is then attached to the absorption apparatus and the stopcocks are turned so that the hydrocyanic acid may flow from the sample bottle through the receiving bulb and out into the cylinder. The 500-cc. bottle containing the sample to be analyzed is next attached, and the liquid hydrocyanic acid is pumped through the apparatus till both are at the same temperature and no loss by volatilization due to the heat of the apparatus is to be feared. The lower stopcock is first closed, then the upper cock. Then the lower stopcock is cautiously opened so that owing to the vapor pressure of the hydrocyanic acid, a very small stream

[1] Presented before the Division of Physical and Inorganic Chemistry at the 70th Meeting of the American Chemical Society, Los Angeles, Calif., August 3 to 8, 1925.

[2] Clennell, "The Chemistry of Cyanide Solutions," 1904, p. 8.

Table for Determination of Per cent of Hydrocyanic Acid by Specific Gravity

Sp. gr.	0° C.	1° C.	2° C.	3° C.	4° C.	5° C.	6° C.	7° C.	8° C.	9° C.	10° C.	11° C.	12° C.	13° C.	14° C.	15° C.	16° C.	17° C.	18° C.	19° C.	20° C.	21° C.	22° C.	23° C.	24° C.	25° C.
0.682	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	100.0
0.683	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	99.7
0.684	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	99.9	99.4
0.685	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	100.0	99.6	99.1
0.686	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	99.7	99.3	98.8
0.687	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	99.9	99.4	99.0	98.5
0.688	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	100.0	99.6	99.1	98.7	98.2
0.689	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	99.7	99.3	98.8	98.4	97.9
0.690	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	99.8	99.4	99.0	98.5	98.1	97.7
0.691	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	100.0	99.5	99.1	98.7	98.2	97.8	97.4
0.692	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	99.7	99.2	98.8	98.4	97.9	97.5	97.1
0.693	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	99.8	99.4	98.9	98.5	98.1	97.6	97.3	96.8
0.694	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	100.0	99.5	99.1	98.6	98.2	97.8	97.4	97.0	96.5
0.695	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	99.7	99.2	98.8	98.3	97.9	97.5	97.1	96.7	96.2
0.696	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	99.8	99.4	98.9	98.5	98.0	97.6	97.2	96.8	96.4	96.0
0.697	....	....	....	....	....	....	....	....	....	....	....	....	....	....	....	99.9	99.5	99.1	98.6	98.2	97.7	97.3	96.9	96.5	96.1	95.7
0.698	....	....	....	....	....	....	....	....	....	....	....	....	....	....	100.0	99.6	99.2	98.8	98.3	97.9	97.5	97.1	96.6	96.2	95.8	95.4
0.699	....	....	....	....	....	....	....	....	....	....	....	....	....	....	99.7	99.3	98.9	98.5	98.0	97.6	97.2	96.8	96.3	95.9	95.5	95.1
0.700	....	....	....	....	....	....	....	....	....	....	....	....	....	99.8	99.4	99.0	98.6	98.2	97.7	97.3	96.9	96.5	96.0	95.6	95.2	94.8
0.701	....	....	....	....	....	....	....	....	....	....	....	....	100.0	99.5	99.1	98.7	98.3	97.9	97.4	97.0	96.6	96.2	95.7	95.3	94.9	94.5
0.702	....	....	....	....	....	....	....	....	....	....	....	....	99.7	99.2	98.8	98.4	98.0	97.6	97.1	96.7	96.3	95.9	95.4	95.0	94.6	94.2
0.703	....	....	....	....	....	....	....	....	....	....	....	99.8	99.4	98.9	98.5	98.1	97.7	97.3	96.8	96.4	96.0	95.6	95.1	95.8	94.3	94.0
0.704	....	....	....	....	....	....	....	....	....	....	99.9	99.5	99.1	98.6	98.2	97.8	97.4	97.0	96.5	96.1	95.7	95.3	94.8	94.5	94.1	93.7
0.705	....	....	....	....	....	....	....	....	....	100.0	99.6	99.2	98.8	98.3	97.9	97.5	97.1	96.7	96.2	95.8	95.4	95.0	94.5	94.2	93.8	93.4
0.706	....	....	....	....	....	....	....	....	....	99.7	99.3	98.9	98.5	98.0	97.6	97.2	96.8	96.4	95.9	95.5	95.1	94.7	94.2	93.9	93.5	93.1
0.707	....	....	....	....	....	....	....	....	99.9	99.4	99.0	98.6	98.2	97.7	97.3	96.9	96.5	96.1	95.6	95.2	94.8	94.4	94.0	93.6	93.2	92.8
0.708	....	....	....	....	....	....	....	100.0	99.6	99.1	98.7	98.3	97.9	97.4	97.0	96.6	96.2	95.8	95.3	94.9	94.5	94.1	93.7	93.3	92.9	92.5
0.709	....	....	....	....	....	....	....	99.7	99.3	98.8	98.4	98.0	97.5	97.1	96.7	96.3	95.9	95.5	95.0	94.6	94.2	93.8	93.4	93.0	92.6	92.2
0.710	....	....	....	....	....	....	99.8	99.4	99.0	98.5	98.1	97.7	97.2	96.8	96.4	96.0	95.6	95.2	94.7	94.3	93.9	93.5	93.1	92.7	92.3	92.0
0.711	....	....	....	....	....	100.0	99.5	99.1	98.7	98.2	97.8	97.4	96.9	96.5	96.1	95.7	95.3	94.9	94.4	94.0	93.6	93.2	92.8	92.4	92.1	91.7
0.712	....	....	....	....	....	99.7	99.2	98.8	98.4	97.9	97.5	97.1	96.6	96.2	95.8	95.4	95.0	94.6	94.1	93.7	93.3	92.9	92.5	92.1	91.8	91.4
0.713	....	....	....	....	99.8	99.4	98.9	98.5	98.1	97.6	97.2	96.8	96.3	95.9	95.5	95.1	94.7	94.3	93.8	93.4	93.0	92.6	92.2	91.8	91.5	91.1
0.714	....	....	....	99.9	99.5	99.1	98.6	98.2	97.8	97.3	96.9	96.5	96.0	95.6	95.2	94.8	94.4	94.0	93.5	93.2	92.7	92.3	91.9	91.6	91.2	90.8
0.715	....	....	100.0	99.6	99.2	98.8	98.3	97.9	97.5	97.0	96.6	96.2	95.7	95.3	94.9	94.5	94.1	93.7	93.3	92.9	92.5	92.1	91.7	91.3	90.9	90.5
0.716	....	....	99.7	99.3	98.9	98.4	98.0	97.6	97.1	96.7	96.3	95.9	95.4	95.0	94.6	94.2	93.8	93.4	93.0	92.6	92.2	91.8	91.4	91.0	90.6	90.3
0.717	....	99.8	99.4	99.0	98.6	98.1	97.7	97.3	96.8	96.4	96.0	95.6	95.1	94.7	94.3	93.9	93.5	93.1	92.7	92.3	91.9	91.5	91.1	90.7	90.3	90.0
0.718	100.0	99.5	99.1	98.7	98.2	97.8	97.4	97.0	96.5	96.1	95.7	95.3	94.8	94.4	94.0	93.6	93.2	92.8	92.4	92.0	91.6	91.2	90.8	90.4	90.0	89.7
0.719	99.6	99.2	98.8	98.4	97.9	97.5	97.1	96.7	96.2	95.8	95.4	95.0	94.5	94.1	93.7	93.3	92.9	92.5	92.1	91.7	91.3	90.9	90.5	90.1	89.8	89.4
0.720	99.3	98.9	98.5	98.1	97.6	97.2	96.8	96.4	95.9	95.5	95.1	94.7	94.2	93.8	93.4	93.0	92.6	92.2	91.8	91.4	91.0	90.6	90.2	89.8	89.5	89.1
0.721	99.0	98.6	98.2	97.7	97.3	96.9	96.5	96.0	95.6	95.2	94.8	94.3	93.9	93.5	93.1	92.7	92.3	91.9	91.5	91.1	90.7	90.3	89.9	89.5	89.2	88.8
0.722	98.7	98.3	97.9	97.4	97.0	96.6	96.2	95.7	95.3	94.9	94.5	94.0	93.6	93.2	92.8	92.4	92.0	91.6	91.2	90.8	90.4	90.0	89.6	89.2	88.9	88.5
0.723	98.4	98.0	97.5	97.1	96.7	96.3	95.9	95.4	95.0	94.6	94.2	93.7	93.3	92.9	92.5	92.1	91.7	91.3	90.9	90.5	90.1	89.7	89.3	89.0	88.6	88.2
0.724	98.1	97.7	97.2	96.8	96.4	96.0	95.6	95.1	94.7	94.3	93.9	93.4	93.0	92.6	92.2	91.8	91.4	91.0	90.6	90.2	89.8	89.4	89.0	88.7	88.3	87.9
0.725	97.8	97.3	96.9	96.5	96.1	95.7	95.2	94.8	94.4	94.0	93.6	93.1	92.7	92.3	91.9	91.5	91.1	90.7	90.3	89.9	89.5	89.1	88.7	88.4	88.0	87.7
0.726	97.4	97.0	96.6	96.2	95.8	95.4	94.9	94.5	94.1	93.7	93.2	92.8	92.4	92.0	91.6	91.2	90.8	90.4	90.0	89.6	89.2	88.8	88.4	88.1	87.7	87.4
0.727	97.1	96.7	96.3	95.9	95.5	95.1	94.6	94.2	93.8	93.4	92.9	92.5	92.1	91.7	91.3	90.9	90.5	90.1	89.7	89.3	88.9	88.5	88.1	87.8	87.4	87.1
0.728	96.8	96.4	96.0	95.6	95.2	94.8	94.3	93.9	93.5	93.0	92.6	92.2	91.8	91.4	91.0	90.6	90.2	89.8	89.4	89.0	88.6	88.2	87.8	87.5	87.1	86.8
0.729	96.5	96.1	95.7	95.3	94.9	94.5	94.0	93.6	93.2	92.7	92.3	91.9	91.5	91.1	90.7	90.3	89.9	89.5	89.1	88.7	88.3	87.9	87.6	87.2	86.8	86.5
0.730	96.2	95.8	95.4	95.0	94.6	94.2	93.7	93.3	92.9	92.4	92.0	91.6	91.2	90.8	90.4	90.0	89.6	89.2	88.8	88.4	88.0	87.6	87.3	86.9	86.6	86.2
0.731	95.9	95.5	95.1	94.7	94.2	93.8	93.4	93.0	92.6	92.1	91.7	91.3	90.9	90.5	90.1	89.7	89.3	88.9	88.5	88.1	87.7	87.3	87.0	86.6	86.3	85.9
0.732	95.6	95.2	94.8	94.3	93.9	93.5	93.1	92.7	92.3	91.8	91.4	91.0	90.6	90.2	89.8	89.4	89.0	88.6	88.2	87.8	87.4	87.1	86.7	86.3	86.0	85.6
0.733	95.3	94.9	94.5	94.0	93.6	93.2	92.8	92.4	91.9	91.5	91.1	90.7	90.3	89.9	89.5	89.1	88.7	88.3	87.9	87.5	87.1	86.8	86.4	86.1	85.7	85.3
0.734	95.0	94.6	94.1	93.7	93.3	92.9	92.5	92.1	91.6	91.2	90.8	90.4	90.0	89.6	89.2	88.8	88.4	88.0	87.6	87.2	86.8	86.5	86.1	85.8	85.4	85.1
0.735	94.6	94.2	93.8	93.4	93.0	92.6	92.2	91.8	91.3	90.9	90.5	90.1	89.7	89.3	88.9	88.5	88.1	87.7	87.3	86.9	86.6	86.2	85.8	85.5	85.1	84.8
0.736	94.3	93.9	93.5	93.1	92.7	92.3	91.9	91.5	91.0	90.6	90.2	89.8	89.4	89.0	88.6	88.2	87.8	87.4	87.0	86.6	86.3	85.9	85.5	85.2	84.8	84.5
0.737	94.0	93.6	93.2	92.8	92.4	92.0	91.6	91.1	90.7	90.3	89.9	89.5	89.1	88.7	88.3	87.9	87.5	87.1	86.7	86.3	86.0	85.6	85.2	84.9	84.5	84.2
0.738	93.7	93.3	92.9	92.5	92.1	91.7	91.2	90.8	90.4	90.0	89.6	89.2	88.8	88.4	88.0	87.6	87.2	86.8	86.4	86.0	85.7	85.3	84.9	84.6	84.2	83.9
0.739	93.4	93.0	92.6	92.2	91.8	91.4	90.9	90.5	90.1	89.7	89.3	88.9	88.5	88.1	87.7	87.3	86.9	86.5	86.1	85.7	85.4	85.0	84.6	84.3	84.0	83.6
0.740	93.1	92.7	92.3	91.9	91.5	91.1	90.6	90.2	89.8	89.4	89.0	88.6	88.2	87.8	87.4	87.0	86.6	86.2	85.8	85.4	85.1	84.7	84.3	84.0	83.7	83.3
0.741	92.8	92.4	92.0	91.6	91.2	90.8	90.3	89.9	89.5	89.1	88.7	88.3	87.9	87.4	87.1	86.7	86.3	85.9	85.5	85.1	84.8	84.4	84.1	83.7	83.4	83.1
0.742	92.4	92.1	91.7	91.3	90.9	90.5	90.0	89.6	89.2	88.8	88.4	88.0	87.6	87.1	86.8	86.4	86.0	85.6	85.2	84.8	84.5	84.1	83.8	83.4	83.1	82.8
0.743	92.1	91.8	91.3	90.9	90.5	90.2	89.7	89.3	88.9	88.5	88.1	87.6	87.3	86.8	86.5	86.1	85.7	85.3	84.9	84.5	84.2	83.8	83.5	83.1	82.8	82.5
0.744	91.8	91.4	91.0	90.6	90.2	89.9	89.4	89.0	88.6	88.2	87.8	87.3	87.0	86.5	86.2	85.8	85.4	85.0	84.6	84.2	83.9	83.5	83.2	82.8	82.5	82.2
0.745	91.5	91.1	90.7	90.3	89.8	89.6	89.1	88.7	88.3	87.9	87.4	87.0	86.7	86.2	85.9	85.5	85.1	84.7	84.3	84.0	83.6	83.2	82.9	82.5	82.2	81.9
0.746	91.2	90.8	90.4	90.0	89.6	89.3	88.8	88.4	88.0	87.6	87.1	86.7	86.3	85.9	85.6	85.2	84.8	84.4	84.0	83.7	83.3	82.9	82.6	82.3	81.9	81.6
0.747	90.9	90.5	90.1	89.7	89.3	89.0	88.5	88.1	87.7	87.3	86.8	86.4	86.0	85.6	85.3	84.9	84.5	84.1	83.7	83.4	83.0	82.6	82.3	82.0	81.6	81.3
0.748	90.6	90.2	89.8	89.4	89.0	88.7	88.2	87.8	87.3	86.9	86.5	86.1	85.7	85.3	84.9	84.6	84.2	83.8	83.4	83.1	82.7	82.3	82.0	81.7	81.4	81.0
0.749	90.3	89.9	89.5	89.1	88.7	88.4	87.9	87.5	87.0	86.6	86.2	85.8	85.4	85.0	84.6	84.3	83.9	83.5	83.1	82.8	82.4	82.0	81.7	81.4	81.1	80.7
0.750	90.0	89.6	89.2	88.8	88.4	88.1	87.6	87.2	86.7	86.3	85.9	85.5	85.1	84.7	84.3	84.0	83.6	83.2	82.8	82.5	82.1	81.7	81.4	81.1	80.8	80.4

flows down through the empty bulb on the absorbing flask, in which space the liquid vaporizes and then bubbles slowly under perfect control through the caustic soda solution, where it is completely absorbed. After the receiving bulb has thus been gradually emptied of the liquid, gentle suction is applied to the lower guard tube, the upper stopcock is opened to connect with the soda-lime tube, which is opened to the air, and a current of air is slowly bubbled through the liquid in the absorption flask, thus removing all traces of hydrocyanic acid from the receiving bulb. The absorber is then detached, the guard tube removed, and after cooling in the balance case the flask and contents are reweighed. The gain in weight represents the hydrocyanic acid absorbed. The entire contents of the absorber are then transferred to a liter flask, made up to volume, and well mixed, after which duplicate 25-cc. portions are titrated in the usual way.

With proper precautions this method fulfils all requirements for accuracy. It is, however, a lengthy operation and it is apparent that its employment must be confined to a well-equipped laboratory, thus precluding its use in the field where frequently these determinations have to be made. In view of these facts a quicker method became necessary.

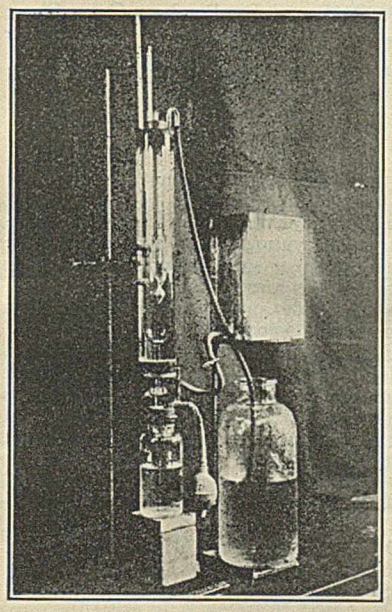


Figure 2—Apparatus for Determination of Specific Gravity of Liquid Hydrocyanic Acid

This need was early recognized by Gray and Hulbirt, who prepared the first set of specific gravity tables to be used in determining the strength of liquid hydrocyanic acid.[3] It was discovered by the writers, however, that some rather wide variations existed between the percentages of hydrocyanic acid determined by the gravimetric method and by the specific gravity method.

The investigation described herein was therefore started in order to obtain a closer agreement between the two methods and to prepare a corrected set of tables.

Principles Involved

The specific gravity tables are applicable to commercial liquid hydrocyanic acid made and distributed in southern California, because this product contains nothing but water in addition to pure hydrocyanic acid. It becomes apparent upon studying the relation between the specific gravity and the percentage of hydrocyanic acid that the method is best adapted to solutions of high concentration and is not at all suited to solutions of very high dilution. Fortunately, however, the dilute solutions are easily analyzed by simple volumetric methods and are of minor importance, since commercial liquid hydrocyanic acid usually contains 96 to 98 per cent hydrocyanic acid.

It is evident here, as in all analyses of high-purity products, that small errors in the observed data will seriously affect the calculated percentage. Therefore ordinary commercial hydrometers by reason of their short and compressed scale, were found to be quite unsuited for this work. Accordingly, a number of specially made, accurate hydrometers were secured and certificates as to their accuracy at 15.6° C. (60° F.) were obtained from the U. S. Bureau of Standards. These instruments measure 25.7 cm. ($10^1/_8$ inches) from tip of stem to point of bulb. The scale reads from 0.650 to 0.750 and contains fifty divisions which extend over a stem length of 106.4 cm. ($4^3/_{16}$ inches), so the space between two graduations occupies 2 mm. ($^1/_{12}$ inch) and therefore it is quite easy to read accurately to the third decimal place. Standard Centigrade thermometers graduated from 0° to 50° in 0.1 degrees were employed for temperature observations.

Not only is accuracy of observation necessary, but it is essential for accurate work that the temperature of the liquid be held constant while the observations are being taken.

Figure 2 shows the apparatus used for this work. The inner cylindrical glass container is surrounded by a glass jacket in which the water may be kept at any desired temperature by a regulated supply from the reservoir at the side. The inner cylinder is closed at its upper end by a perforated rubber stopper, and a capillary tube inserted therein maintains atmospheric pressure in the interior without evaporation of the liquid, while a glass stopcock at the lower end retains the liquid in the cylinder for observation as long as desired.

Preparation of Pure Liquid Hydrocyanic Acid

It is evident that the liquid hydrocyanic acid used for this work must be absolutely pure, so commercial hydrocyanic acid of 96 to 98 per cent purity was slightly acidified with sulfuric acid and was then redistilled. This distillate was allowed to stand over calcium chloride for a few days, after which it was again distilled, yielding anhydrous hydrocyanic acid free from impurities. From this stock supply, by dilution and by subsequent analyses, the various percentages of liquid needed for the investigation were prepared.

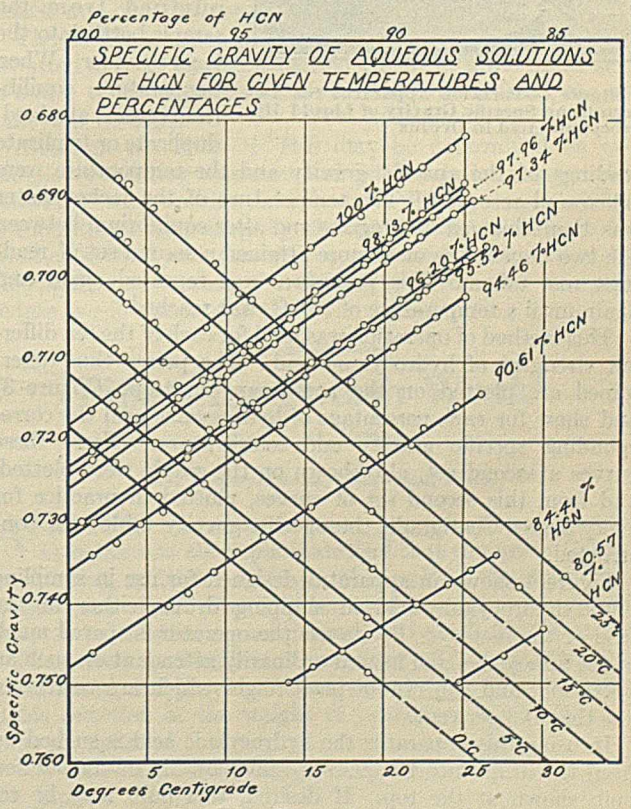


Figure 3

Gravimetric Analysis of Samples

The gravimetric method already described was used for this work. The buret was carefully checked and the corrections so obtained were applied to the work. Titrations were

[3] University of California, *Bull.* **308** (June, 1919).

so arranged that each one used between 40 and 50 cc. of silver nitrate, in which region the buret corrections were almost negligible.

The standard silver nitrate (approx. 0.1*N*) was very carefully standardized by precipitation with a known slight excess of 0.1 *N* hydrochloric acid followed by filtration on a Gooch crucible and subsequent weighing in the usual way. These determinations were made in triplicate and the average was taken. Since the maximum divergence between the weights of silver chloride found was only a milligram and since the samples of hydrocyanic acid used for subsequent analysis weighed 10 grams or more, the error in the analyses of hydrocyanic acid, due to standardization of the silver nitrate solution would not exceed 0.00127, when expressed in percentage of hydrocyanic acid in the sample analyzed.

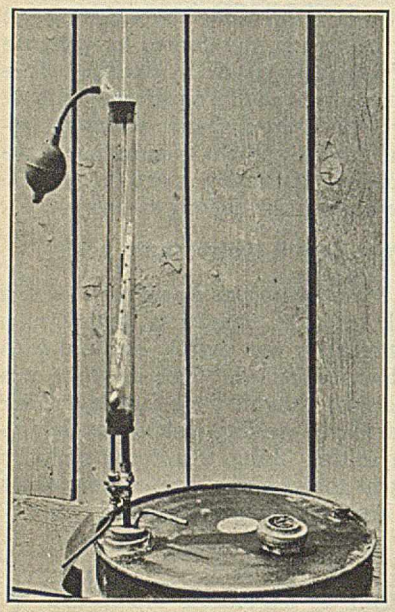


Figure 4—Portable Apparatus for Determining Specific Gravity of Liquid Hydrocyanic Acid in Drums

Determination of Specific Gravity

The various samples prepared and analyzed as indicated were cooled to 0° C. The jacket was filled with water at this temperature and the sample of liquid hydrocyanic acid was pumped from the sample bottle into the inner cylinder. When temperature equilibrium was attained, duplicate or triplicate readings of the specific gravity and the temperature were taken and recorded. The temperature of the jacket water was then changed 1.5 degrees and after equilibrium between the two liquids was once more attained a second set of readings was taken. This procedure was repeated again and again until a temperature of 25° C. was reached.

This method of operation was used for each of the ten different strengths of hydrocyanic acid. The points thus determined are plotted on the accompanying graph (Figure 3) and show for each percentage of hydrocyanic acid the corresponding specific gravity and temperature. From these curves a second set, also shown on the graph, were plotted, and from this second set of curves, plotted in practice for every degree Centigrade, the specific gravity table was constructed.

Figure 4 shows an apparatus designed for use in sampling liquid hydrocyanic acid in shipping drums either in the field or the factory. By its use the operator is spared much of the annoyance and hazard ordinarily attendant on such an operation, and can obtain percentages which are correct to less than 0.2 per cent.

In using this apparatus the hydrocyanic acid is sucked up from the drum into the glass cylinder by use of the suction bulb shown at the top. If desired, this bulb may be replaced by a bicycle pump, the discharge hose from which is attached to the right-angled copper tube which passes through the rubber stopper at the right of the vertical tube.

If a sample of the liquid is desired for any purpose it can be drawn from the glass cylinder through the small copper tube emerging from the bottom of the cylinder at the left.

Determination of Hydrocyanic Acid in Gaseous Mixtures[1]

By Gilbert E. Seil

The Koppers Company Laboratories, Mellon Institute, Pittsburgh, Pa.

THE determination of hydrocyanic acid in gaseous mixtures has always been a rather long and tedious operation requiring careful manipulation and unusually good technic. The method which is here described reduces the time necessary for a determination to a few minutes, requires very little apparatus, and after a little practice can be followed by an unskilled worker with satisfactory results. This method has been checked in the laboratory of The Koppers Company at the Seaboard By-Product Coke Plant against the method generally used. Synthetic mixtures of known amounts of hydrocyanic acid were analyzed with unusually accurate results.

Theory

This method depends upon the following facts:

1—The reaction between hydrocyanic acid and iodine in a sodium bicarbonate solution yields cyanogen iodide and hydriodic acid. The function of the excess of sodium bicarbonate is to neutralize the hydriodic acid as it is formed.

2—A mixture of cyanogen iodide and hydriodic acid yields hydrocyanic acid and iodine in acid solution.

3—Hydrogen sulfide and iodine yield hydriodic acid and sulfur. This reaction is irreversible under the conditions of this method.

4—The writer has found no other constituent of any gaseous mixture, which he has analyzed, which absorbs iodine in sodium bicarbonate solution and then liberates iodine upon acidification of the products of absorption.

The following reactions explain these facts:

$$HCN + I_2 + NaHCO_3 = NaI + CNI + CO_2 + H_2O \quad (1)$$
$$CNI + HI + HCl = HCl + HCN + I_2 \quad (2)$$
$$H_2S + I_2 = 2HI + S \quad (3)$$

Usual Method

Pass the gas at the rate of about 85 liters (3 cu. ft.) per hour through four bottle washers, each containing about 100 cc. of 15 per cent pure sodium hydroxide solution. The volume of the gas to be taken for analysis depends on the hydrocyanic acid content. At least 570 liters (20 cu. ft.) should be passed where the hydrocyanic acid content is only 0.0458 mg. per liter (2 grains per 100 cu. ft.). Wash the solution from the bottles, make up to 500 cc. and take a 50-cc. sample. Add the precipitated lead carbonate, filter, and wash. Titrate the filtrate, which should be free from sulfur, with 0.1 *N* silver nitrate, using a few drops of 10 per cent potassium iodide as an aid to the determination of the end point.

$$\frac{\text{Cc. } 0.1\,N\ AgNO_3 \times 10 \times 0.0054 \times 15.43 \times 100}{\text{Cu. ft. of gas (cor.)}} = \text{Grains HCN per 100 cu. ft.}$$

$$\text{or} \quad \frac{\text{Cc. } 0.1\,N\ AgNO_3 \times 10 \times 0.0054}{\text{Liters of gas}} = \text{Mg. HCN per liter}$$

The method is a little simpler on gas containing only a small amount of hydrogen sulfide, such as outlet gases from the wet purification process. On gases high in hydrogen sulfide the latter might be removed first, provided it is done without any loss of hydrocyanic acid.

Preparation of Lead Carbonate—Make a solution of lead nitrate and add excess sodium carbonate solution. Allow the lead carbonate precipitate to settle and test the supernatant clear liquid for complete precipitation by adding a small quantity of sodium carbonate solution. Wash the precipitate three or four times by decantation with cold water

[1] Received August 18, 1925.

until free of soluble salts. Add enough of the lead carbonate prepared in this way to the 50-cc. sample so that some of the white lead carbonate in excess remains unused in the flask.

Proposed Method

Solutions

0.1 *N* IODINE—This is made approximately tenth normal although the exact strength need not be known.

STANDARD SODIUM THIOSULFATE SOLUTION—1 cc. equals 0.2288 mg. per liter (10 grains of HCN per 100 cu. ft.) of gas on a 500-cc. gas sample. It is made by diluting 84.75 cc. of standard 0.1 *N* sodium thiosulfate solution to 1 liter. This solution must be prepared daily.

STARCH SOLUTION—A dilute starch solution is saturated with sodium bicarbonate. This solution must be prepared daily.

DILUTE HYDROCHLORIC ACID—A solution containing 1 part of concentrated HCl to 8 parts of water.

Apparatus

(1) A specially constructed Tutwiler, as shown in the accompanying drawing. Although the usual Tutwiler buret with the gas chamber enlarged to 500 cc. could be used, this modification with a larger solution reservoir increases the volume of starch solution remaining after the sample is taken. A large volume of starch solution is desirable owing to the large volume of gas to be scrubbed.

(2) A 10- or 25-cc. buret.

(3) A receptacle such as an Erlenmeyer flask or a beaker.

Determination of Amount of Dilute HCl to Be Used to Acidify

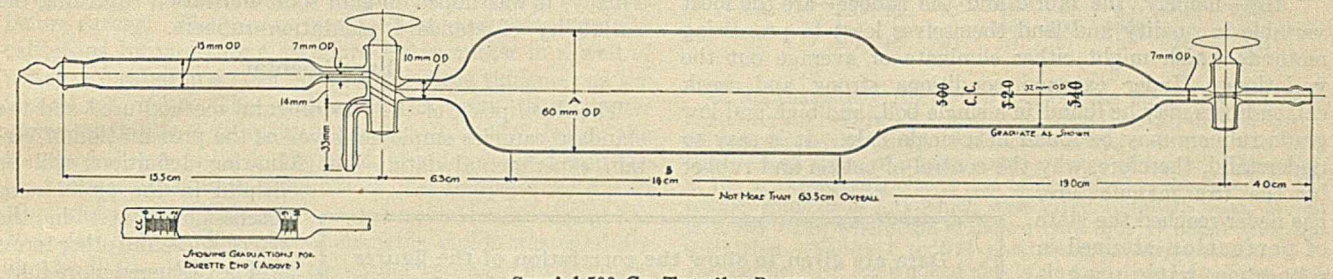
Fill the Tutwiler with the starch-bicarbonate solution to the 540 cc. mark. Remove the solution and titrate with the dilute hydrochloric acid solution to decided acidity, note the amount of hydrochloric acid solution used, and then use this same quantity of acid for each determination at the point where the colorless solution is acidified.

Sampling

Two methods have been used for filling the modified Tutwiler with the gas sample. The first, or usual, method requires filling the Tutwiler with a starch-bicarbonate solution first and then displacing this with the gaseous mixture to be analyzed. The second method, which is preferred here, is simpler and necessitates filling the modified Tutwiler with water, displacing all the water with the gas sample and purging for a few minutes with gas. Both methods of sampling are equally good. In the first method any absorbed hydrocyanic acid is held in the solution, which does not leave the modified Tutwiler apparatus. In the second method there can be no loss of hydrocyanic acid, as the gas which enters the top of the apparatus has the true amount of hydrocyanic acid in it and purges the gas which has lost hydrocyanic acid from the apparatus. The gas volume is now adjusted in the usual manner with a leveling bottle so that it is exactly 500 cc.

Procedure

Add the iodine solution carefully, with violent shaking, after each addition, until the starch solution just turns blue. No reading need be taken at this point. It is important to note, however, that a large over-titration at this point tends to cause a reaction between the sodium bicarbonate present and the iodine, yielding NaIO which liberates iodine on acidification. Wash the blue solution from the Tutwiler into a receptacle, either with distilled water or with the sodium bicarbonate solution, by allowing the wash solution to enter the gas inlet of the Tutwiler and flow over the walls of the Tutwiler, leaving it at the bottom cock. If the blue color fades at this point, add a small amount of dilute iodine until the color reappears. Titrate with standard solution *exactly* to the disappearance of the blue and take the reading of the buret. Acidify with the amount of hydrochloric acid solution which was previously determined as necessary to give an acid reaction and allow the acid solution to stand for 0.5 to 1 minute. If a blue color appears, there is hydrocyanic acid present, and the solution should be titrated *exactly* to the disappearance of the blue color with standard solution.



Special 500-Cc. Tutwiler Buret

The difference in cubic centimeters of the two buret readings multiplied by 10 equals the grains of HCN per 100 cu. ft. when a 500-cc. sample is taken for analysis, or 1 cc. equals 0.2288 mg. of HCN per liter.

The method never gives low results, but if the original titration in the Tutwiler is carried too far or if too much acid is added to the colorless solution when it is acidified, the results will be high.

Although the HCN + H_2S may be determined on one sample by titrating with standard iodine solution using starch saturated with sodium bicarbonate, the hydrogen sulfide is then determined alone by titrating, using acid starch for another sample and the hydrocyanic acid finally taken by difference, the chances of error are too great and this procedure is not recommended.

Pipets for Potash Work[1]

By C. M. Bible

READ PHOSPHATE CO., NASHVILLE, TENN.

ANALYSTS who make frequent determinations of potash as potassium chloroplatinate find that the use of pipets transferring multiples of 19.38 ml. simplifies the calculation of per cent K_2O. There is no need for reference tables, errors in calculation are minimized, and much time is saved.

Three sizes give sufficient range for all potash materials encountered, and provide the individual chemist much choice in his selection of the weight of potassium chloroplatinate to be precipitated.

The following figures illustrate the convenience in using the pipets:

Per cent potash in materials	Ml. solution used	Gram sample represented	To convert wt. K_2PtCl_6 to % K_2O divide by
Up to 4	58.14	0.5814	0.03
4 to 20	38.76	0.3876	0.02
Above 20	19.38	0.1938	0.01

[1] Received August 29, 1925.

Effect of Accelerators on Cure and Quality of Various Rubbers[1]

By R. P. Dinsmore and A. O. Zimmerman

THE GOODYEAR TIRE & RUBBER CO., AKRON, OHIO

Data are given to show the correlation of the figures for cure and quality between different accelerators in the same type of mixing, and with a number of different rubbers. It is found that the variation on the whole is not great; that where a variation exists there is no apparent correlation between the behavior of different accelerators, or with any of these and a straight sulfur mix. Variability due to cure is greater than that due to quality. Variation in mixings with some accelerators appears to be higher than with others.

An experimental procedure is outlined and a quality index figure developed, which is shown to be more reliable for a limited number of tests than tensile or tensile product. A brief discussion of the causes of variation and the need for more extensive investigation is also presented.

IT IS a fact that has caused tire technologists considerable concern that the two most important constituents of a tire—namely, the fabric and the rubber—are the most variable in quality and lend themselves least to processing methods which might either eliminate or average out the variations. Under extreme conditions strong and weak cotton fibers may be found in a single boll, and high and low grade rubbers may be found in a single bale. It is easy to understand, therefore, why the control of cotton and rubber by the tire manufacturer has never reached the state of perfection attained in connection with practically every other tire ingredient.

It has long been recognized that certain wild rubbers have a more rapid rate of cure than others, and that, in the plantation varieties, brown crepe is likely to be slower than pale crepe or smoked sheets. These things, while constituting some draw-back to the promiscuous interchange of rubbers in a given formula, do not cause the rubber compounder much concern. It is a fact, however, that two different lots of the same type of rubber may vary widely as to rate of cure, and even after the cure is adjusted a difference in the physical properties, and therefore in the quality of the finished product, may exist. This produces an element of uncertainty which is a source of continuous worry to the rubber compounder.

Owing to a recognition of these facts the Rubber Division of the AMERICAN CHEMICAL SOCIETY has appointed a committee whose chief function is to outline a method by which the quality of rubber may be determined. Undoubtedly, one of the impelling motives behind this move was to make it possible for rubber chemists to tell the rubber growers exactly what kind of rubber they want, and to give them a means of measuring against a standard the quality of the rubber which they produce, thereby enabling them to take steps to eliminate much of the variation which now exists. Unfortunately, it was soon discovered that there was a distinct lack of agreement among rubber chemists regarding the properties which they require in rubber. Moreover, it was found that, even if such an agreement can be obtained, it is no simple matter to fix a formula which will accurately classify various rubbers for use with different types of accelerators of vulcanization.

It was the purpose of this investigation to discover whether there could be found any correlation in the properties obtained by the use of different accelerators in the same type of mix. It was desired to ascertain how much of the difference encountered could be attributed to change in the rate of cure and how much to other factors which affect only the quality. Finally, it was hoped to gain some indication regarding the variability of standard plantation rubbers.

Experimental

The description of the experimental method used and the standard samples employed involves the presentation of certain experimental data. The following definitions will be helpful in the preliminary discussion. Later in the paper, these and other terms will be discussed more fully.

Best Cure. The time of vulcanization at a given temperature, at which essential physical properties approach the most satisfactory balance, both with respect to each other and to their own values after aging.

Stiffness Index (S. I.). A measure of the resistance to stretching of the rubber. (The authors originally used the term "variability index," but have adopted S. I. as being more truly descriptive of the property measured.) For pure gum and sulfur mixes this property is expressed as the increase in load necessary to change the elongation from 600 to 800 per cent. For accelerated mixes the load-increase from 500 to 700 per cent is used.

The need was recognized of distinguishing carefully between variables inherent in the rubber and those introduced by manipulation and testing. Great care was taken, therefore, to give identical treatment to all samples of rubber.

It was desired to test a number of commercially used accelerators and also a mixing in which no accelerator was introduced. It was also desired to test a number of rubbers, which were selected as being variable with one accelerator, against all the rest. In order to place the accelerators originally on the same footing, it was decided to prepare a well-blended rubber from the two common types produced by plantations—namely, smoked sheets and pale crepe. In order to do this, rubber was selected from ten different estates, and ten bales were taken at random from a lot from each estate. Five pounds were then taken from each bale and the 5-pound samples carefully blended. Each bale was broken down separately on a mill before the 5-pound sample was taken. The standard rubbers thus obtained were designated as blended rubber, and a formula was worked out for each accelerator to give the same stiffness of the stress-strain curve at a best cure of 1 hour. In all cases, except for mercaptobenzothiazole, which was cured at 125° C. (20 pounds), the standard cure was 141° C. (40 pounds), and in order to expose any unforeseen testing error a large batch of rubber was mixed according to the Hex formula. This was sheeted out on a calender to the proper thickness for laboratory test, the sheets were rolled up in holland, and a

[1] Presented before the Division of Rubber Chemistry at the 69th Meeting of the American Chemical Society, Baltimore, Md., April 6 to 10, 1925

sheet of this standard batch was cured with every rubber test that was made.

Mixing of the laboratory batches was done on a 16-inch mill with rolls 8 inches in diameter, with a ratio of 1:1.25. The cooling water used was maintained at a temperature of 54.5° C. (130° F.), in a supply reservoir, and was distributed to the mill through a 0.5-inch pipe under a pressure of 95 pounds per square inch.

The mixing specifications were as follows: weight of batch, 500 grams; mill gage, 2.5 mm.; rubber time, 6 minutes; total time, 10 minutes. After mixing, the batch was sheeted out to the proper thickness and allowed to age for 24 hours before curing. The presses used for this work were carefully calibrated by inserting a standard thermometer in a well of mercury located in a steel block of the same thickness as the laboratory mold. The reading of the press thermometer corresponding to a temperature of 141° C. (287° F.) on the standard thermometer in the block was determined, and the presses were thereafter operated at this temperature for all 40-pound cures. The same procedure was carried out for 20-pound cures. The time of changing molds was carefully standardized. After curing, the sheets were aged for 48 hours, with uniform exposure of the sheet surfaces in a rack where the temperature varied between the limits of 23.6° and 26.7° C. (75° and 80° F.).

The sheets were then died out with a die having the same proportions as No. 10 recommended by the Physical Testing Committee of the Rubber Division on page 13 of their 1924 report. The test specimens were carefully gaged and tested on an autographic stress-strain machine, upon which there is an adjustment for gage so that elongation is charted against kilograms per square centimeter. The average precision of this machine is within 2 per cent. The temperature of the testing room was also maintained between the limits of 23.6° and 26.7° C. (75° and 80° F.).

A qualitative comparison of the tear resistance of different test sheets was found to be readily obtainable by hand. The method is to cut the test sheet in the direction of the calender grain, and to tear the cut, thus started, for a sufficient distance to get an impression of the average resistance to tear. The same method is applied to other sheets with which the comparison is made. For example, a series of cures varying in time by 15-minute increments may be compared in this way and the cure giving maximum tear resistance easily determined.

Quantitative comparisons may be made by using a narrow strip and substituting testing machine grips for the hands. The same procedure is applied after aging. In general the cure which gives maximum tear resistance before aging will give very close to maximum after aging. This differs from any other important physical property of rubber.

Data

Owing to the number of lots used, letters were employed to designate each lot of rubber, the same letters being used in many cases for both smoked sheets and pale crepe. In all cases, therefore, the data have been labeled with the kind of rubber as well as the lot designation. The accelerators used are designated as follows:

Mer—mercaptobenzothiazole
TPG—triphenylguanidine
DPG—diphenylguanidine
Vul—Vulcone
Thio—thiocarbanilide
Hex—hexamethylenetetramine
PG—pure gum and sulfur mix

Table A—Composition of Various Mixings for Blended Rubbers
(Pounds per 100 pounds rubber)

Name of Accelerator	Pale Crepe Accelerator	Pale Crepe Sulfur	Pale Crepe Zinc Oxide	Smoked Sheets Accelerator	Smoked Sheets Sulfur	Smoked Sheets Zinc Oxide
Thio	2.75	7.00	6.00	2.75	6.50	6.00
Hex	0.90	3.00	6.00	0.90	3.00	6.00
DPG	0.40	2.75	6.00	0.40	2.75	6.00
Vul	0.35	3.00	6.00	0.35	3.25	6.00
TPG	3.00	4.00	6.00	1.75	4.00	6.00
Mer	0.35	3.20	6.00	0.35	3.20	6.00
PG	..	10.00	..	..	10.00	..

Table B—Stress-Strain Data and Stiffness Index for Blended Rubbers

Accelerator	Best cure	S. I.	Load 500	Load 600	Load 700	Tensile	Elongation
Pale Crepe							
Thio	1:00/40	56	25	42	81	150	805
Hex	1:00/40	53	21	38	74	145	815
DPG	1:00/40	56	22	40	78	169	835
Vul	1:00/40	51	21	37	72	140	815
TPG	1:00/40	55	21	37	76	168	840
Mer	1:00/20	49	22	38	71	129	805
			(600	700	800)		
PG	2:15/40	27	18	26	45	112	945
Smoked Sheets							
Thio	1:00/40	61	29	49	90	130	745
Hex	1:00/40	54	23	41	77	166	840
DPG	1:00/40	60	24	45	84	155	815
Vul	1:00/40	51	22	39	73	146	825
TPG	1:00/40	55	24	43	79	160	830
Mer	1:00/20	55	25	42	80	167	835
			(600	700	800)		
PG	2:15/40	33	20	31	53	121	945

Of approximately thirty-two lots of pale crepe sampled only eight were tested in all types of mixings over a range of cures. Of approximately thirty-five lots of smoked sheets sixteen were tested in all types of mixings over a range of cures. Therefore, in the accompanying charts and tables the data are based on the smaller number of lots which were given complete tests, except in a few cases where the standard cure only is taken into consideration. Tables I to VII give complete stress-strain, S. I., and curing data for smoked sheets in each type of mixing, each table referring to a different type of mixing. Tables VIII to XIV give the same data for pale crepe.

Table XV gives a comparison of Schidrowitz's slope, for a series of cures, against stiffness index at the best cure for smoked sheets and for pale crepe. In both cases the slope figure which is italicized indicates the best cure for that particular rubber.

Charts 1 and 11 show for each accelerator how the S. I. of the various lots of rubber fluctuates at the standard cure. Charts 3 and 13 show the same variation at the best cure for each rubber. Charts 2 and 12 show how the S. I. for each lot of rubber varies with different accelerators at the standard cure. Charts 4 and 14 give the same data at the best cure for each rubber. Charts 5 and 15 show how the time of best cure varies in each type of mixing for the different lots of rubber. Charts 6 and 16 show how the time of best cure for each lot of rubber is affected by the different accelerators. Charts 7 and 17 show the increase in S. I. with the time of cure. Charts 8 and 18 show distribution curves of the S. I. at the standard cure for each type of mixing. Chart 9 shows the complete stress-strain curves for three lots of pale crepe, and indicates how the S. I. and slope are determined and where the reference points used by de Vries and Sanderson come with respect to the stress-strain curve. (There is no Chart 10, charts being numbered this way for ease in comparing.)

Testing Criteria

It is obvious that a study of rubber variation must deal with properties which are of fundamental importance, if conclusions drawn therefrom are to be of value. It is unfortunate that there is no general agreement regarding such properties, and it is doubtless due to this fact that the practical service test holds its present dominant place in the rubber industry. It is impossible for the authors of this paper to accept the criteria for rubber which have been adopted by other investigators. It becomes needful, therefore, to justify the selection of other standards.

From the standpoint of the manufacturer of rubber goods, the properties which are important in the raw materials are those which affect the ease of manufacture and the quality of the finished product. In this paper the discussion will be limited to those properties which affect final quality. Therefore, in the testing of crude rubber to determine its value for manufactured rubber products, only those properties should be considered which are known to determine the quality of the finished article. It may be desirable to investigate other properties in an attempt to establish a relationship with the final quality. But until such a relationship is determined the use of such properties as a means for evaluating, controlling, or classifying rubbers, is useless, misleading, and, in all probability, worse than no control at all.

With this clearly in mind it will be apparent that the use of the terms "cure" and "quality" in the classification of

Table I—High and Low Smoked Sheets, Cured with Pure Gum at 40 Pounds

Lot	Cure Hrs. and min.	S. I.	100	200	300	400	500	600	700	800	900	Tensile	Elong.	State of Cure
Blended	2:00	29	5	7	9	11	14	19	28	48	85	96	925	Under
	2:15	33	5	7	9	12	15	20	31	53	95	121	945	Best
	2:30	41	5	8	10	13	16	24	37	65	119	124	910	Good plus
HHH	2:00	31	5	7	9	11	15	20	30	51	88	90	910	Under
	2:15	34	5	7	9	12	16	21	32	55	99	113	925	Good minus
	2:30	36	5	7	9	13	18	26	40	72		114	880	Best
KKK	2:00	28	5	6	8	11	14	20	28	48	83	108	955	Under
	2:15	31	5	7	9	12	15	21	30	52	91	104	925	Good minus
	2:30	38	5	7	9	12	17	23	35	61	114	120	910	Best
MMM	2:00	52	5	8	11	15	20	28	45	80		118	870	Good minus
	2:15	56	5	8	11	16	21	30	47	86		133	870	Best
	2:30	71	6	9	12	17	24	35	57	106		148	860	Over
LLL	2:00	31	4	6	8	10	15	19	29	50	88	100	925	Under
	2:15	34	4	6	8	11	15	20	31	54	92	104	925	Good minus
	2:30	44	5	7	9	12	18	25	38	69		108	880	Best
GGG	2:00	30	5	6	8	11	14	20	29	50	86	100	920	Under
	2:15	34	5	7	9	12	15	21	31	55	100	117	925	Good minus
	2:30	43	5	8	10	13	18	25	39	68		117	895	Best
A	2:00	39	5	7	9	12	17	23	37	62	115	126	915	Good minus
	2:15	40	6	8	10	13	18	26	38	66	119	130	915	Best
	2:30	61	7	9	12	17	23	32	51	93		165	895	Over
RRR	2:00	39	5	7	9	13	17	24	36	63	110	110	900	Good minus
	2:15	42	5	7	10	13	18	25	38	67	120	133	920	Best
	2:30	56	5	8	11	15	21	30	47	86		147	890	Over
SS	2:00	56	6	9	12	16	21	30	47	86		122	860	Best
	2:15	67	6	9	12	16	23	33	53	100		144	865	Over
	2:30	56	6	9	14	19	27	40	68	128		158	835	Over
ZZ	2:00	39	5	7	10	13	17	23	35	62	112	112	900	Good minus
	2:15	46	5	8	11	14	19	26	40	72	124	126	905	Best
	2:30	56	6	9	11	15	21	31	47	87		136	875	Over
XXX	2:00	53	5	8	11	14	20	29	46	82	145	145	900	Best
	2:15	62	5	8	11	16	23	33	52	95		137	860	Over
	2:30	79	6	9	12	18	25	37	61	116		166	860	Over
YY	2:00	36	5	7	9	12	17	22	34	58	100	100	900	Good minus
	2:15	42	5	7	10	13	18	23	36	65		121	890	Best
	2:30	49	6	8	11	14	19	26	41	75		142	895	Good plus
PPP	2:00	49	5	7	10	14	19	27	43	76		122	885	Best
	2:15	59	5	7	10	15	20	29	49	88		134	875	Over
	2:30	68	5	8	11	16	23	34	57	102		154	850	Over
SSS	2:00	53	5	7	10	15	21	28	45	81		131	880	Good plus
	2:15	65	5	8	11	16	23	33	51	98		132	850	Over
	2:30	75	5	9	12	17	25	37	60	112		158	860	Over
UUU	2:00	65	6	9	12	17	24	34	55	99		120	835	Good plus
	2:15	69	6	9	12	18	25	36	60	105		105	800	Over
	2:30	88	6	9	13	19	27	43	69	131		156	800	Over
WWW	2:00	52	6	8	10	14	19	28	46	80		118	870	Best
	2:15	59	6	8	11	15	21	31	50	90		136	870	Over
	2:30	66	6	9	12	17	25	37	58	103		143	860	Over
NNN	2:00	50	5	8	10	15	19	28	44	78		116	865	Best
	2:15	63	6	9	11	16	23	33	53	96		138	860	Over
	2:30	78	6	9	12	17	26	38	62	116		160	845	Over

rubbers is without significance, unless these properties are related in a known way to the properties of the finished article. Hence, the state of vulcanization or cure of any rubber tested must be the technically correct or "best" cure, which corresponds to that producing the most durable finished article, because there is no known relationship between the properties at best cure and those at other cures. Likewise, the properties selected for comparison at the best cure must be those which forecast the durability of the finished product.

For reasons to be discussed later, the stiffness of the rubber, as shown by the stress-strain curve, and the tear resistance have been selected as the two most significant properties. The former definition of best cure may now be modified to read—the time of vulcanization at a given temperature, at which stiffness and tear resistance approach the most satisfactory balance, both with respect to each other and to their own values after aging. One year's normal aging should be a satisfactory criterion for most work.

It is now necessary to explain why tear and stiffness were selected as the most important physical properties by which to determine variation. It will be sufficient in this paper to point out that in a large number of articles made from rubber the ability to resist tear, whether produced by external contact or internal shear, is of greatest importance, and the stiffness or resistance to deformation has a profound influence on the character of the rubber. These properties also fulfil the condition of being subject to variation, both by changes in cure and changes in rubber. Tensile strength is undoubtedly important, but there is a serious question whether most rubber articles, stressed to point of failure, do not fail from tear before the ultimate tensile strength is reached. It is also noteworthy that it is difficult, if not impossible, to produce a rubber compound having high tear resistance and stiffness without at the same time having high tensile.

Certain physical properties of rubber may be neglected, either because they are practically constant (for a given amount of pigmentation) or because they are functions of cure. Such properties are elasticity, its reciprocal—hysteresis—and permanent set. Other properties which have been used or suggested as criteria for rubber quality are tensile strength, elongation, tensile product, energy of resilience, Schidrowitz's slope, and coefficient of vulcanization. It has already been stated that tensile is a correlative property with tear resistance and stiffness. Table C shows the relationship between S. I. and tensile. The relationship for S. I. and ultimate elongation is in the same order of variability. The figures given in the table represent the average for all lots of rubber of each type for which the stress-strain data were obtained at the best cure.

Table C—Relation between S. I. and Tensile

Rubber	Hex	Mer	Thio	Vul	DPG	TPG	PG
Smoked sheets	0.41	0.39	0.35	0.35	0.36	0.39	0.37
Pale crepe	0.32	0.33	0.39	0.34	0.32	0.34	0.22

This table shows a fairly consistent relationship between tensile and S. I. when enough tests are taken to give a good average tensile. It indicates that tensile and S. I. vary in the same direction, at least in the neighborhood of the best cure. It is worth noting that a considerable number of tests are necessary to determine tensile accurately, whereas S. I. can be determined with precision on the stress-strain curve from one test. Therefore, in a sense, it is unnecessary to

Table II—High and Low Smoked Sheets, Cured with Hexamethylenetetramine at 40 Pounds

Lot	Cure Hrs. and min.	S. I.	100	200	300	400	500	600	700	800	Tensile	Elong.	State of Cure
Blended	:45	39	5	7	10	13	18	31	57	99	123	845	Under
	1:00	54	6	8	11	16	23	41	77	137	166	840	Best
	1:15	71	6	9	13	18	28	51	99	176	176	800	Over
HHH	:45	44	5	7	10	13	20	36	64	109	122	825	Good minus
	1:00	60	6	8	11	16	26	47	86		140	790	Best
	1:15	75	6	9	13	19	30	57	105		166	785	Over
KKK	:45	49	5	7	9	12	18	32	58	101	120	830	Good minus
	1:00	58	5	8	11	16	25	46	83		140	795	Best
	1:15	73	5	8	12	18	28	54	101		168	790	Over
MMM	:45	51	6	7	10	14	22	40	73		115	785	Best
	1:00	72	6	9	12	18	29	55	101		147	770	Good plus
	1:15	87	6	10	14	22	36	67	123		150	740	Over
LLL	:45	48	5	7	10	13	21	38	69		104	775	Good minus
	1:00	64	6	8	12	16	27	49	91	153	162	815	Best
	1:15	75	6	10	13	19	32	58	107		171	785	Good plus
GGG	:45	44	5	7	9	12	19	35	63	109	126	830	Good minus
	1:00	62	5	7	10	16	25	47	87	149	154	810	Best
	1:15	79	6	9	13	20	31	59	110		180	795	Over
A	:45	48	4	7	10	14	21	37	69	120	151	850	Best
	1:00	74	5	8	11	16	26	52	100	177	188	810	Good plus
	1:15	92	5	8	12	18	31	65	123		157	740	Over
RRR	:45	50	6	7	10	14	22	40	72	124	138	825	Best
	1:00	70	7	8	12	18	29	55	99		156	785	Good plus
	1:15	86	7	9	14	20	35	65	121		175	770	Over
SS	:45	61	5	8	11	16	25	47	86		136	785	Best
	1:00	84	6	10	14	20	33	63	117		162	760	Over
	1:15	97	7	10	15	23	38	73	135		170	745	Over
ZZ	:45	52	6	8	10	14	22	41	74		118	785	Best
	1:00	70	6	9	12	18	29	53	99		148	775	Good plus
	1:15	84	6	9	14	20	33	63	117		168	765	Over
XXX	:45	60	5	8	10	16	26	48	86		130	785	Best
	1:00	74	7	9	13	19	31	57	105	176	178	805	Good plus
	1:15	100	7	10	16	24	41	78	141		174	740	Over
YY	:45	47	5	7	10	14	21	37	68	121	148	845	Good minus
	1:00	66	6	9	12	17	27	50	93		126	755	Best
	1:15	78	6	9	13	18	30	57	108		173	785	Good plus
PPP	:45	55	5	7	10	15	24	44	79		130	795	Best
	1:00	73	6	8	12	18	30	56	103		144	765	Good plus
	1:15	88	6	9	14	21	35	67	123		175	770	Over
SSS	:45	59	5	7	11	16	25	46	84		134	790	Best
	1:00	82	6	8	12	19	33	62	115		150	750	Good plus
	1:15	93	6	9	15	26	39	72	132		188	765	Over
UUU	:45	52	5	7	9	14	23	42	75		118	785	Best
	1:00	70	5	8	11	17	29	53	99		158	795	Over
	1:15	91	5	9	15	22	37	71	128		170	750	Over
WWW	:45	54	6	8	11	15	23	43	77	125	125	800	Best
	1:00	77	7	9	13	19	31	58	108		146	760	Over
	1:15	92	7	10	15	22	37	71	129		144	720	Over
NNN	:45	52	5	7	10	15	23	42	75	127	130	810	Best
	1:00	71	5	8	12	18	30	56	101		144	770	Over
	1:15	88	6	9	13	21	35	67	123		172	765	Over

use tensile as a measure of quality. Used alone it is unsatisfactory, because as time of cure increases tensile increases considerably beyond the point where maximum tear resistance and best aging properties are secured. Therefore the best aging cannot be selected by the tensile figure. Moreover, rubber test specimens usually fail on account of imperfections, and therefore a number of tests are required to get a good average of tensile.

The same arguments apply to ultimate elongation, except that it decreases with cure instead of increasing.

Tensile product is a somewhat better figure, because it usually passes through a maximum at a point nearer to best cure than does tensile. Its maximum, however, is usually beyond the point where maximum tear resistance and best aging properties exist.

Energy of resilience has been shown by Wiegand[2] to be only a measure of reënforcing effect of pigments. Different crudes and different states of cure give about the same "concavity factor"—i. e., deviation from Hooke's law. This simply means that energy of resilience is no more a sensitive index of rubber quality than tensile product, for, as Wiegand says, tensile product "exactly represents twice the energy of resilience of the sample, had it followed Hooke's law."

Schidrowitz's slope is not sufficiently sensitive to change in rubber properties. Examination of the data in Table XV shows that rubbers having a considerable displacement of the stress-strain curve may give exactly the same value of slope, whereas they have a quite different value for S. I. at the best cure. Typical examples are smoked sheets, Lots 2S, 1A and 3N; and pale crepe, Lots X and W. This would indicate that slope figure is not sufficiently sensitive to indicate appreciable differences in stiffness of rubbers. This is further confirmed by Chart 9, which shows two rubbers, V and W, for which the slope figures are nearly alike but for which the stress-strain curves have a considerable displacement and the S. I. values are over 25 per cent apart. A later table (Table E) will show still greater discrepancies. Reference to Chart 17 shows that if this difference were due to cure it would amount to about 20 minutes at 40 pounds. Since these rubbers are taken at the best cures the differences are due to quality, but the comparison is made to show that the differences are appreciable. Lots W and T, on the other hand, are nearly identical as far as stress-strain curves are concerned; yet the slope figures show a difference of 16 per cent, which is one of the greatest differences shown in this property; the S. I. is almost identical for both. We would conclude, therefore, that Schidrowitz's slope frequently fails to indicate important differences where they exist and in the other cases indicates differences which are not important. The writers confirm the de Vries' findings that slope does not remain constant with varying cures. Their results, on the contrary, show that slope decreases with increase of time of cure, at least in the vicinity of the best cure.

Coefficient of vulcanization has been shown by other investigators[3,4] to be an unsatisfactory criterion.

Hence we find that if we admit stiffness and tear resistance to be important rubber variables none of the other commonly known properties is satisfactory as a criterion of quality. At this point a few words regarding de Vries' method of determining state of cure may be of interest.[5] He uses a fixed

[2] This Journal, **17**, 623 (1925).

[3] Shepard and Krall, This Journal, **14**, 951 (1922).

[4] Sebrell and Vogt, *Ibid.*, **16**, 793 (1924).

[5] "Estate Rubber," p. 338.

Table II—High and Low Smoked Sheets, Cured with Vulcone at 40 Pounds

Lot	Cure Hrs. and min.	S. I.	100	200	300	400	500	600	700	800	Tensile	Elong.	State of Cure
Blended	:45	47	5	8	10	13	20	36	67	117	143	840	Under
	1:00	51	6	8	10½	14	22	39	73	127	146	825	Good to best
	1:15	58	6	9	11	15	24	44	82	145	145	800	Good plus
HHH	:45	40	6	7	9	13	19	33	59	100	138	870	Under
	1:00	50	6	8	10	15	23	40	73	127	154	845	Best
	1:15	50	6	9	11	15	23	41	73	127	137	815	Good plus
KKK	:45	41	5	7	9	13	20	34	61	105	144	865	Under
	1:00	48	6	8	11	14	22	39	70	122	146	835	Good minus
	1:15	51	6	8	11	15	23	40	74	128	154	835	Best
MMM	:45	50	5	8	11	15	23	40	73	123	151	845	Good minus
	1:00	56	6	9	12	16	25	45	81	139	158	830	Best
	1:15	58	6	9	12	17	27	47	85	145	155	815	Over
LLL	:45	39	5	8	10	14	20	33	59	99	130	850	Good minus
	1:00	45	6	9	11	15	22	37	67	115	158	840	Best
	1:15	48	6	9	12	16	23	40	71	123	152	840	Good plus
GGG	:45	42	5	7	9	13	19	34	61	106	119	825	Under
	1:00	47	6	8	11	15	22	39	69	119	147	840	Best
	1:15	48	6	8	11	15	23	39	71	126	157	845	Good plus
A	:45	43	5	7	10	13	20	35	63	109	121	825	Good minus
	1:00	49	5	8	10	14	22	38	71	125	136	820	Best
	1:15	49	5	8	10	15	23	39	72	127	150	835	Over
RRR	:45	48	6	8	11	15	21	38	69	119	135	830	Best
	1:00	56	6	9	12	16	23	43	79	137	164	840	Good plus
	1:15	56	6	9	12	16	24	44	80	141	159	825	Over
SS	:45	61	5	8	11	15	27	48	88	149	158	815	Best
	1:00	68	6	9	13	19	31	55	99	168	170	800	Good plus
	1:15	71	6	9	13	19	31	57	102	173	176	805	Over
ZZ	:45	46	5	7	10	14	21	37	67	120	158	855	Good minus
	1:00	55	5	8	11	15	24	43	79	140	164	835	Best
	1:15	59	5	8	11	15	24	45	83	146	172	835	Over
XXX	:45	56	6	8	11	16	25	45	81	137	137	800	Best
	1:00	61	6	9	12	17	28	50	89	150	150	800	Good plus
	1:15	61	6	9	12	17	28	50	89	152	162	815	Over
YY	:45	44	5	7	10	13	20	34	64	112	150	860	Good minus
	1:00	48	5	7	10	15	21	37	69	121	156	850	Best
	1:15	49	5	7	10	15	22	38	71	125	156	845	Good plus
PPP	:45	53	6	8	12	16	25	43	78	132	151	830	Good minus
	1:00	59	6	8	12	17	26	46	85	145	152	800	Best
	1:15	62	6	8	12	17	26	49	88	152	157	815	Good plus
SSS	:45	54	6	8	11	16	25	44	79	136	145	815	Best
	1:00	64	6	9	12	17	26	47	90	155	162	810	Good plus
	1:15	66	6	9	12	17	27	51	93	158	158	800	Over
UUU	:45	54	5	8	11	16	25	43	79	135	144	815	Best
	1:00	60	6	9	12	17	27	48	87		146	790	Good plus
	1:15	63	6	9	12	18	28	50	91		138	785	Over
WWW	:45	52	6	8	11	16	24	42	76	129	139	815	Good minus
	1:00	54	7	9	12	17	25	44	79		122	780	Best
	1:15	57	7	9	12	17	26	46	83	140	158	825	Good plus
NNN	:45	46	6	8	11	15	22	37	68	115	123	815	Good minus
	1:00	50	6	8	11	16	25	41	75	130	136	810	Best
	1:15	53	6	8	11	16	25	43	78	136	136	800	Good plus

reference point—130 kg. per sq. cm. at 890 per cent elongation, cure 96 minutes ± 10.5 per cent at 151° C. for smoked sheets, and 115.7 minutes ± 6.7 per cent at 151° C. for pale crepe—to determine the rate of cure of a pure gum mixing containing 7.5 per cent of sulfur. If the stress-strain curve falls below this point the rubber is classed as slow curing, and if above, fast curing. From the questionnaire he sent out to the American rubber chemists he concludes[6] that a variation of 20 to 25 per cent in the time of cure is satisfactory. This may have been based upon the opinion which the authors of this paper, among others, held at that time—that variations in the rate of cure with crude rubbers were largely eliminated by the use of accelerators, and that very little rubber was used commercially in pure gum mixings. Certainly, such a variation in a pure gum mixing would be too great for good manufacturing practice. Since de Vries' reference point represents a bad overcure for most of the rubbers tested by the writers, they have little data in its immediate vicinity, but they can show that marked displacement of the stress-strain curves of different rubbers is apparent at the best cure for each. For this purpose a load of 80 kg. was selected, and the corresponding elongations tabulated. The data are given in Table D.

An examination of these data shows conclusively that pure gum mixings cured at their best cures do not pass through any fixed point in the stress-strain diagram. According to de Vries' method, one would expect the pale crepe to be very much undercured with respect to the smoked sheets, whereas as a matter of fact all the rubbers selected in this table are at their best cures, the difference being in some inner quality of the rubber. Even considering smoked sheets alone, the curves, although much nearer together, are far from passing through a given point. There is a maximum difference of 765 to 870 per cent on the elongation axis. Lot 3M, for example, at 80 kg., only changes from 755 to 800 per cent elongation while going from a 2:30 to a 2:00-hour cure. Therefore, tremendous differences in time of cure would be necessary to account for the differences in these stress-strain curves. It remains to be shown that a satisfactory measure of stiffness can be obtained from the stress-strain curve for rubber.

Table D—Displacement of Stress-Strain Curve at Best Cure

Smoked Sheets				*Pale Crepe*			
Lot	Best cure Hrs. and min.	Elong. at 80 kg.	S. I.	Lot	Best cure Hrs. and min.	Elong. at 80 kg.	S. I.
3N	2:00	805	50	2B	2:15	925	21
3W	2:00	800	52	W	2:00	945	18
3U	2:00	765	65	2C	2:15	930	21
3S	2:00	800	53	Y	2:15	910	22
3P	2:00	810	49	X	2:00	920	24
2Y	2:15	835	42	N	2:15	900	25
3X	2:00	795	53	2A	2:15	930	21
2Z	2:15	820	46	T	2:00	965	19
2S	2:00	790	56	Bl.R.	2:15	885	27
3R	2:15	830	42				
1A	2:15	810	40				
3G	2:30	830	43				
3L	2:30	825	44				
3M	2:15	790	56				
3K	2:30	845	38				
Bl.R.	2:15	870	33				

Considering the diverse uses to which rubber is put, it would seem that we should be interested in the entire stress-strain curve or at least in a stiffness figure which is a good average for the entire curve. Probably, for many purposes, a direct comparison of the stress-strain curves is the most

[6] "Rubber on the Market and in the Factory," p. 67.

Smoked Sheets

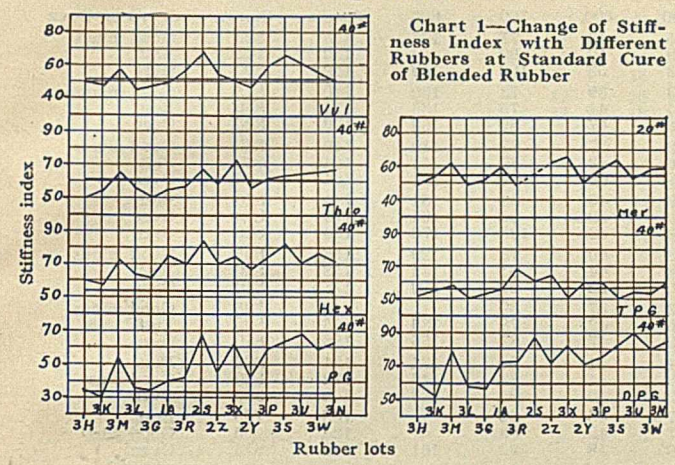


Chart 1—Change of Stiffness Index with Different Rubbers at Standard Cure of Blended Rubber

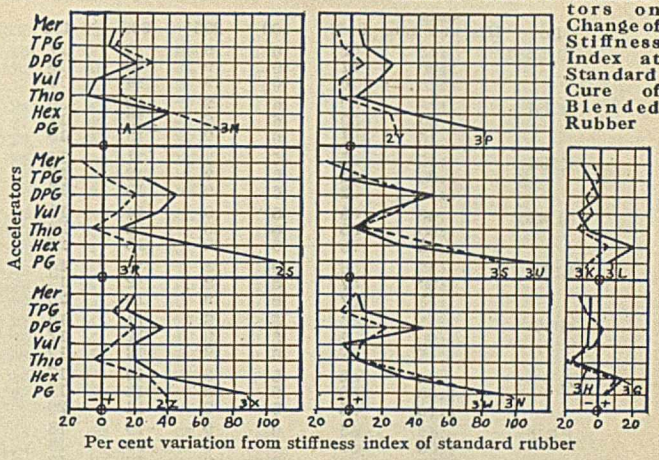


Chart 2—Effect of Accelerators on Change of Stiffness Index at Standard Cure of Blended Rubber

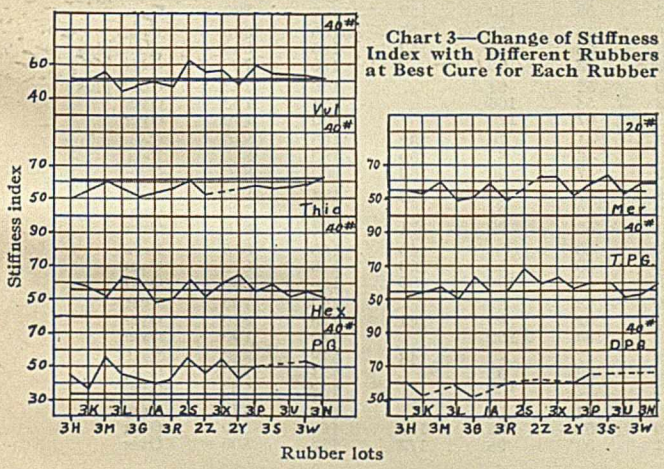


Chart 3—Change of Stiffness Index with Different Rubbers at Best Cure for Each Rubber

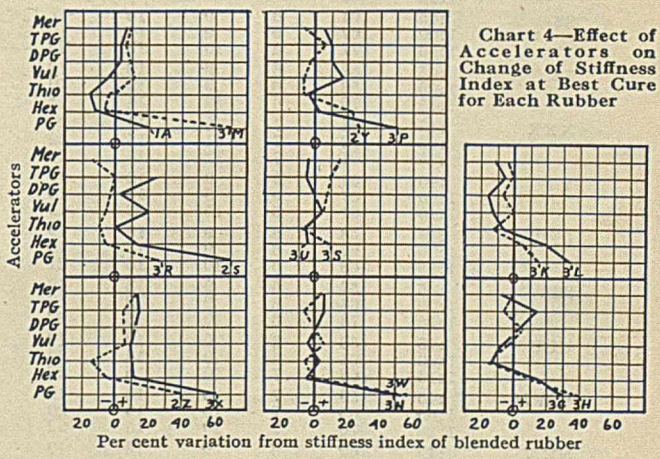


Chart 4—Effect of Accelerators on Change of Stiffness Index at Best Cure for Each Rubber

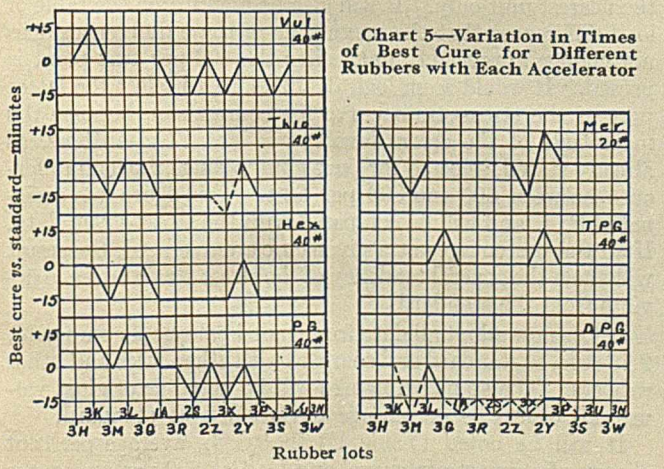


Chart 5—Variation in Times of Best Cure for Different Rubbers with Each Accelerator

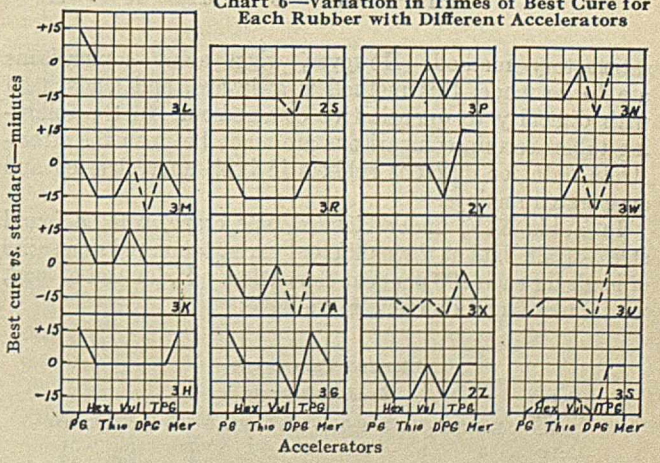


Chart 6—Variation in Times of Best Cure for Each Rubber with Different Accelerators

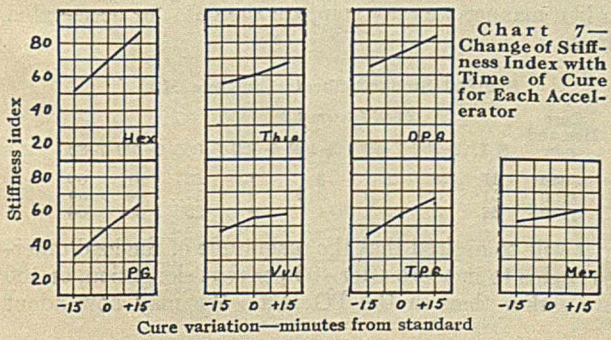


Chart 7—Change of Stiffness Index with Time of Cure for Each Accelerator

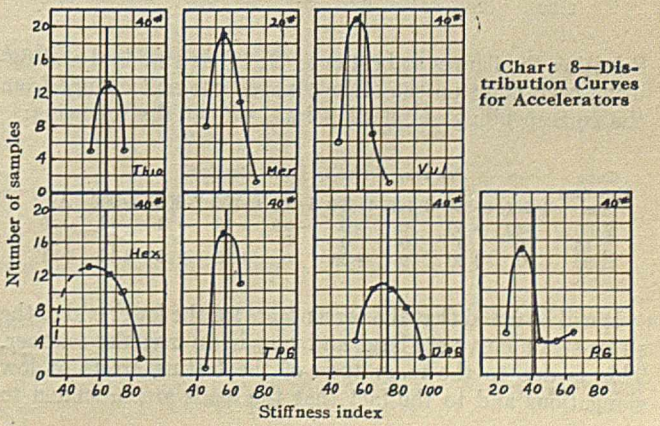


Chart 8—Distribution Curves for Accelerators

Table IV—High and Low Smoked Sheets, Cured with Thiocarbanilide at 40 Pounds

Lot	Cure Hrs. and min.	S. I.	100	200	300	400	500	600	700	800	Tensile	Elong.	State of Cure
Blended	:45	52	6	9	12	17	25	43	77	135	155	825	Good minus
	1:00	61	6	9	13	18	29	49	90		130	745	Best
	1:15	70	6	9	14	19	33	58	103	159	159	800	Over
HHH	:45	50	6	8	12	16	23	39	73	130	140	815	Good minus
	1:00	50	6	8	12	17	25	41	75	135	174	850	Best
	1:15	61	6	9	13	19	28	47	89	160	179	825	Over
KKK	:45	45	5	8	11	15	22	37	67	119	146	840	Good minus
	1:00	54	6	9	12	17	26	43	80	141	154	815	Best
	1:15	62	6	9	13	19	28	48	90	161	164	805	Over
MMM	:45	59	6	9	14	19	29	49	88	151	164	820	Best
	1:00	65	6	10	15	20	30	52	95	164	174	815	Over
	1:15	70	6	10	15	22	33	56	103	178	194	820	Over
LLL	:45	50	5	8	11	16	23	40	73	129	158	845	Good minus
	1:00	57	5	8	12	17	24	44	81	144	158	820	Best
	1:15	67	6	9	13	20	30	52	97	170	178	810	Over
GGG	:45	46	5	8	11	15	23	37	69		112	785	Good minus
	1:00	52	6	9	12	17	26	42	78	139	155	825	Best
	1:15	58	6	9	13	19	29	47	87	155	188	840	Over
A	:45	52	6	8	12	17	24	41	76	134	134	800	Best
	1:00	56	6	8	13	18	26	44	82	146	172	830	Good plus
	1:15	65	6	9	14	20	29	50	94	168	168	800	Over
RRR	:45	55	6	9	13	18	27	45	82		138	795	Best
	1:00	56	6	9	13	18	27	46	83		138	795	Good plus
	1:15	62	6	9	13	19	30	50	92	161	182	825	Over
SS	:45	61	6	9	13	18	28	49	89	151	162	815	Best
	1:00	67	6	9	14	19	30	52	97	167	182	820	Good plus
	1:15	77	6	10	15	22	33	59	110	189	206	820	Over
ZZ	:45	53	6	9	13	18	26	43	79	137	166	840	Best
	1:00	58	6	9	13	19	27	46	85	149	185	845	Good plus
	1:15	70	6	10	14	20	30	53	100		170	795	Over
XXX	:45	64	7	10	14	20	30	52	94		146	785	Good plus
	1:00	73	7	11	15	22	33	58	106		151	765	Over
	1:15	81	7	12	17	25	39	67	120		166	760	Over
YY	:45	51	6	9	12	17	25	41	76	132	160	840	Good minus
	1:00	57	6	9	12	18	28	46	85	150	180	835	Best
	1:15	61	6	10	13	19	29	47	90	159	200	850	Over
PPP	:45	58	6	9	13	19	28	47	86	146	184	850	Best
	1:00	62	6	9	13	19	29	49	91		142	780	Over
	1:15	68	6	10	15	21	31	53	99	171	178	810	Over
SSS	:45	57	6	9	13	18	27	46	84	146	155	815	Best
	1:00	64	6	9	13	19	29	50	93	160	178	820	Over
	1:15	73	6	10	15	22	33	57	106	185	185	800	Over
UUU	:45	58	6	9	13	19	29	48	87		145	795	Best
	1:00	64	6	9	14	20	31	52	95	161	178	820	Over
	1:15	68	7	10	15	22	34	55	102		172	790	Over
WWW	:45	59	7	10	13	19	28	47	87	148	178	840	Best
	1:00	65	7	10	14	20	30	52	95		151	785	Over
	1:15	70	7	10	15	22	33	57	103		172	795	Over
NNN	:45	62	6	9	13	19	29	51	91		118	745	Best
	1:00	65	6	9	13	20	30	52	95	163	190	830	Over
	1:15	66	6	10	14	21	32	53	98	173	176	805	Over

satisfactory method. However, when many comparisons are to be made, this method is awkward, and lends itself with difficulty to quantitative comparison. In the following tables certain comparisons are made between the stress-strain data for different rubbers in both unaccelerated and accelerated mixings.

In Table XIV, under blended pale crepe, will be found stress-strain data at three different cures, tabulated as a series of loads for each 100 per cent elongation. If, instead of load, we tabulate load differences, we have:

Blended Pale Crepe

Cure Hrs. and min.	*Load Increments* 1–200	2–300	3–400	4–500	5–600	6–700	7–800	8–900
2:00	3	1	2	2	4	7	15	31
2:15	2	2	2	2	5	8	19	42
2:30	2	3	2	3	5	10	24	50

Selecting the figures at best cure (2:15) as standard and figuring each point on the other cures as per cent change from the corresponding standard points, we get the following:

Cure Hrs. and min.	*Per cent Deviation from Standard* 1–200	2–300	3–400	4–500	5–600	6–700	7–800	8–900	Av.
2:00	+50	−50	0	0	−20	−13	−21	−26	−10
2:15	0	0	0	0	0	0	0	0	0
2:30	0	+50	0	+50	0	+25	+26	+19	+21

It will be noted that the percentages for the lower end of the stress-strain curve are large and vary in an irregular manner. This is due to the magnitude of the testing errors at low elongations and to the fact that the loads are tabulated to the nearest unit only. It will also be noted from the table of load differences that the magnitude of these differences does not change appreciably until after the 500 per cent point is passed. It would seem logical, therefore, to select the latter part of the stress-strain curve for comparison, because the magnitude of the errors involved is less. The authors, as already stated, selected for pure gum mixings the load difference between 600 and 800 per cent. This figure was designated S. I. and will be compared with the stress-strain data. If all the percentages at a given cure are averaged, the result will show the general tendency of the stress-strain curve to deviate from the standard.

Let us now adopt all data for blended pale crepe, pure gum, 2:15 cure, as standard and compare with other cures and other rubbers. The standard figures will be noted as original values, all others as percentage deviation from standard.

It will be noted (Table E) that S. I., average per cent change of stress-strain curve, and load at 800 per cent agree very closely. All other figures vary erratically.

In like manner we may compare the data for accelerated mixings.

Blended Smoked Sheets (Vulcone Mix)

Cure Hrs. and min.	S. I.	*Load Increments* 1–200	2–300	3–400	4–500	5–600	6–700	7–800
:45	47	3	2	3	7	16	31	50
1:00	51	3	2.5	3.5	8	17	34	54
1:15	58	3	2	4	9	20	38	63

Here it will be noticed that the magnitude of the load differences begins to increase after 400 per cent elongation, or 100 points earlier than in the PG mix. We may now adopt

Table V—High and Low Smoked Sheets, Cured with Diphenylguanidine at 40 Pounds

Lot	Cure Hrs. and min.	S. I.	100	200	300	400	500	600	700	800	Tensile	Elong.	State of Cure
Blended	:45	49	5	8	11	14	20	37	69	120	136	825	Good minus
	1:00	60	5	9	11	16	24	45	84	145	155	815	Best
	1:15	68	6	9	12	18	27	50	95	161	161	800	Good plus
HHH	:45	53	6	9	12	16	24	42	77	135	144	810	Good minus
	1:00	61	6	9	13	18	27	49	88		144	785	Best
	1:15	69	6	9	13	19	29	52	98		168	795	Over
KKK	:45	49					23	39	72		145	830	Good minus
	1:00	55					26	44	81		178	845	Best
	1:15	68					28	54	96		182	820	Over
MMM	:45	72	6	10	13	19	30	55	102	173	177	805	Over
	1:00	78	6	10	14	21	33	60	111	189	196	810	Over
	1:15	89	6	10	15	22	36	67	125		202	790	Over
LLL	:45	54	5	8	11	15	23	42	77	135	164	840	Good minus
	1:00	59	6	9	12	17	26	46	85	148	172	830	Best
	1:15	75	6	9	13	19	29	55	104	172	172	800	Over
GGG	:45	52	5	8	10	15	23	42	75	131	164	845	Best
	1:00	58	5	8	11	16	25	45	83	145	156	815	Good plus
	1:15	70	5	9	12	18	29	53	99	172	182	810	Over
A	:45	62	6	9	11	16	25	45	87	151	174	830	Good plus
	1:00	72	6	9	12	18	29	53	101	177	200	825	Over
	1:15	82	6	9	13	19	31	59	113	197	217	820	Over
RRR	:45	61	6	9	12	17	25	45	86	151	166	820	Best
	1:00	72	6	9	13	18	29	53	101	177	182	810	Over
	1:15	77	7	10	14	20	33	59	110	191	194	805	Over
SS	:45	75	5	8	13	19	31	57	106		173	790	Good plus
	1:00	87	6	9	14	20	33	63	120		196	790	Over
	1:15	94	6	9	14	21	35	69	129		202	785	Over
ZZ	:45	62	6	8	12	16	25	45	87		140	785	Best
	1:00	72	7	9	13	18	29	53	101	173	180	810	Over
	1:15	86	7	10	14	20	33	62	119		200	795	Over
XXX	:45	79	6	9	13	20	32	60	111		166	775	Good plus
	1:00	82	6	9	14	21	33	62	115		181	785	Over
	1:15	91	7	10	15	23	37	68	128		192	780	Over
YY	:45	60	6	8	12	16	25	45	85	149	175	830	Best
	1:00	71	6	9	13	19	28	51	99	175	188	815	Over
	1:15	85	6	10	14	21	32	61	117		200	795	Over
PPP	:45	66	6	9	13	19	29	51	95	164	164	800	Best
	1:00	75	6	9	14	20	31	58	106		170	790	Over
	1:15	84	6	10	15	21	35	64	119	182	182	800	Over
SSS	:45	74	6	9	13	19	31	57	105		167	785	Good plus
	1:00	85	7	10	14	21	35	65	120		192	790	Over
	1:15	90	7	11	15	23	37	67	127		210	795	Over
UUU	:45	80	5	9	13	20	33	61	113	188	190	805	Good plus
	1:00	90	6	9	14	21	35	67	125		202	790	Over
	1:15	94	6	10	15	22	37	70	131		196	775	Over
WWW	:45	66	7	9	13	18	28	52	94		156	795	Good plus
	1:00	80	8	11	15	21	33	61	113		178	785	Over
	1:15	83	8	11	16	23	36	65	119		180	780	Over
NNN	:45	77	6	10	13	19	32	59	109		176	790	Good plus
	1:00	85	7	10	14	20	34	63	119		178	775	Over
	1:15	87	7	10	15	21	35	65	122		186	775	Over

the blended smoked sheets, 1:00 cure, as the standard, and make the same comparisons as before (Table F).

Here again there is close agreement between S. I., average per cent change of stress-strain curve, and load at 700 per cent, whereas all other figures are erratic. It would seem that the load at 700 per cent for accelerated mixings and the load at 800 per cent for pure gum mixings would be just as significant as S. I. However, the latter eliminates zero errors in setting of pen for autographic chart, and is practically as simple to determine.

The results of these comparisons are of obvious significance. If stiffness is considered an essential characteristic of rubber, and it is admitted that displacement of the stress-strain curve denotes changes in stiffness, criteria suggested by other investigators are misleading and the index figure adopted by the authors is satisfactory. Needless to say, the property of stiffness was not selected by the authors upon purely theoretical considerations. Practical experience has shown it to be one of the most important of rubber properties.

Discussion of Results

One important reversal of the writers' former opinions regarding the properties of accelerated stocks is that the use of an accelerator does not necessarily make times of best cure uniform. It is true that fast and slow curing rubber as determined in a pure gum mix may give the same time of cure in an accelerated mix. In fact, it was on this account that the erroneous impression was formed that accelerated mixings are more uniform in cure than pure gum mixings. On the other hand, two rubbers giving the same time of cure for pure gum mixings may give different times of cure in

Table E—Comparison of Data for Unaccelerated Mixings

Rubber	Cure Hrs. and min.	S. I.	Av. % change of S. S. curve	Tensile	Ultimate elong.	Tensile product	Load at 800%	Energy of resilience	Coeff. of vulcanization	Schidrowitz slope
Blended pale crepe	2:15	0/27	0	0/112	0/945	0/106	0/45	0/216.8	0/2.56	0/34
	2:00	−19	−10	−13	+2	−12	−16	− 4	−19	+18
	2:30	+26	+21	0	− 3	− 4	+20	+ 3	+17	0
Pale crepe, CC	2:15	−22	−20	− 3	+ 3	0	−18	−35	− 6	−
Smoked sheets, 3M	2:15	+107	+100	+19	− 8	+ 1	+91	+19	+31	0
Blended smoked sheets	2:15	+22	+19	+ 8	0	+ 8	+18	+15	+ 8	+ 6

Table F—Comparative Data for Accelerated Mixings

Rubber	Cure Hrs. and min.	S. I.	Av. % change of S. S. curve	Tensile	Ultimate elong.	Tensile product	Load at 700%	Energy of resilience	Coeff. of vulcanization
Blended smoked sheets, Vul	1:00	0/50	0	0/146	0/825	0/120	0/73	0/268.0	0/1.35
	:45	− 8	−11	− 2	+ 2	+ 1	− 8	+1/2	−19
	1:15	+14	+14	− 1	− 3	− 3	+12	− 2	+18
Pale crepe, 2A TPG	1:00	−14	− 8	+11	+ 4	+16	−12	+10	+28
Smoked sheets, 2S Vul	:45	+20	+24	+ 8	− 1	+ 8	+21	+ 9	− 4

Table VI—High and Low Smoked Sheets, Cured with Triphenylguanidine at 40 Pounds

Lot	Cure Hrs. and min.	S. I.	100	200	300	400	500	600	700	800	Tensile	Elong.	State of Cure
Blended	:45	45	6	9	11	15	21	36	66	113	106	805	Good minus
	1:00	55	6	9	12	16	24	43	79	137	160	830	Best
	1:15	63	6	9	12	17	26	47	89	155	193	845	Good plus
HHH	:45	42	5	8	10	14	20	34	62		102	790	Good minus
	1:00	52	6	9	12	17	25	42	77	134	134	800	Best
	1:15	61	7	10	13	19	28	49	89	156	178	825	Over
KKK	:45	45	5	7	10	14	21	36	66		112	795	Good minus
	1:00	55	5	8	11	17	24	42	79	139	154	820	Best
	1:15	61	5	8	11	17	25	45	86	152	168	820	Over
MMM	:45	44	5	7	10	14	21	37	65	113	120	815	Under
	1:00	58	6	8	12	16	25	45	83	143	152	815	Best
	1:15	61	6	9	13	17	27	47	88		130	770	Good plus
LLL	:45	42	6	8	11	15	21	35	63	109	119	820	Good minus
	1:00	51	7	9	12	17	25	41	76	133	152	825	Best
	1:15	59	7	10	13	18	27	47	86	150	175	830	Good plus
GGG	:45	43	5	7	10	13	20	34	63	110	120	820	Good minus
	1:00	53	6	8	11	16	24	41	77		98	740	Good minus
	1:15	62	6	9	12	17	26	47	88	154	154	800	Best
A	:45	40	6	8	10	14	20	33	60		74	735	Good minus
	1:00	56	6	9	12	17	25	43	81		136	790	Best
	1:15	62	6	9	12	17	27	47	89		142	785	Good plus
RRR	:45	45	5	7	10	13	20	35	65		102	780	Good minus
	1:00	55	6	8	12	16	25	43	80	138	166	835	Best
	1:15	63	6	9	13	18	27	48	90		184	755	Good plus
SS	:45	54	5	8	10	17	25	43	79		96	735	Good minus
	1:00	68	6	9	12	19	29	51	97	167	176	810	Best
	1:15	75	6	9	13	20	31	57	106		174	790	Over
ZZ	:45	44	5	8	10	14	21	36	65		92	760	Good minus
	1:00	60	6	9	12	17	25	45	85		114	750	Best
	1:15	66	6	10	13	19	27	49	93	164	167	805	Over
XXX	:45	49	5	8	10	15	23	40	72		107	775	Under
	1:00	63	6	9	13	18	27	49	90	153	165	815	Best
	1:15	71	7	10	14	20	31	55	102		160	780	Over
YY	:45	40	6	8	10	14	20	33	60	104	104	800	Under
	1:00	51	7	9	12	16	23	40	74	130	144	820	Good minus
	1:15	58	7	10	13	18	25	45	83	146	184	845	Best
PPP	:45	45	5	7	10	14	22	37	67		110	790	Under
	1:00	60	6	8	12	17	25	45	85	145	156	815	Best
	1:15	70	6	9	13	18	29	52	99		142	765	Good plus
SSS	:45	45	5	7	10	15	22	37	67	116	116	800	Good minus
	1:00	60	6	8	12	17	27	45	87		127	770	Best
	1:15	70	6	9	14	19	30	54	100	171	180	810	Good plus
UUU	:45	42	4	6	8	12	18	33	60		86	765	Under
	1:00	52	5	7	10	15	23	41	75		116	775	Best
	1:15	66	5	8	12	17	28	50	94	159	162	805	Good plus
WWW	:45	42	5	7	10	14	21	35	63		78	740	Good minus
	1:00	53	6	8	11	16	24	42	77	133	166	845	Best
	1:15	67	6	8	12	18	28	51	95		160	795	Good plus
NNN	:45	44	5	7	10	14	22	37	66		94	765	Under
	1:00	59	6	8	12	17	26	46	85		120	770	Best
	1:15	70	7	9	13	19	29	53	99	171	176	805	Over

accelerated mixings (see Lots 3H and 3K in pure gum, Vulcone, and mercapto mixings).

No one of the mixings selected can be used as a criterion of cure or quality for any of the rest (see Charts 1, 3, 11, and 13). There is more variation due to cure than to quality exclusive of cure, but there is an important amount of variation due to quality alone.

Examination of Charts 1, 3, 11, and 13 shows that the lots of smoked sheets tested give a higher average S. I. than the pale crepe lots. The smoked sheets is more variable from all causes than pale crepe, also more variable in quality in the pure gum mix. On the other hand, a higher percentage of pale crepe rubbers had best cure off-standard. On the whole, pale crepe is more uniform than smoked sheets, but it is unfortunately uniformly low. Of the mixings used, TPG is the most uniform throughout, and Hex next.

It occurred to the writers that high and low quality might correspond with short and long times of best cure, respectively. Table G, however, shows that there is no such relationship for smoked sheets.

Table G—Relation of Quality to Best Cure

Accelerator	High S. I. Lot	High S. I. Best cure	Low S. I. Lot	Low S. I. Best cure
Vul	3M	1:00	3R	:45
Thio	3M	:45	3H	1:00
Hex	2Y	1:00	1A	:45
PG	3X	2:00	3K	2:30
Mer	3S	1:00	3R	1:00
TPG	2S	1:00	3L	1:00
DPG	3P	:45	3G	:45

This shows that no fixed relationship exists, although a general survey of all the data indicates that there is a tendency for fast curing rubbers to be higher in quality than the slow curing ones. This, of course, is particularly true of pure gum.

Of approximately thirty-two lots sampled, the following percentages for each type of mixing have their best cures within a few minutes of the standard cure for blended rubber:

Mixing	Mer	DPG	Hex	TPG	PG	Vul	Thio
			Pale Crepe				
Per cent	53	33	38	53	41	53	41
			Smoked Sheets				
Per cent	34	20	42	77	45	54	17

It is thus shown that the amount of cure variation shown in these rubbers, which should be representative of those re-

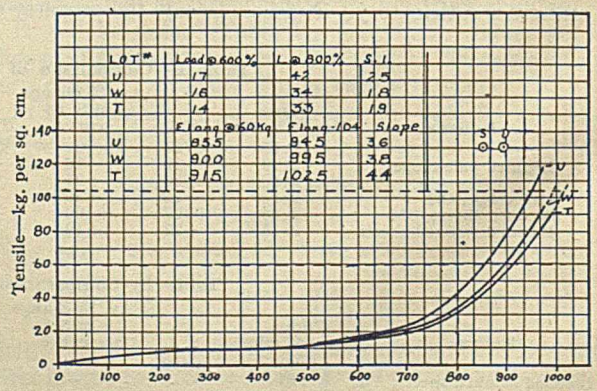


Chart 9—Pale Crepe: Stiffness Index *vs.* Slope

Pale Crepe

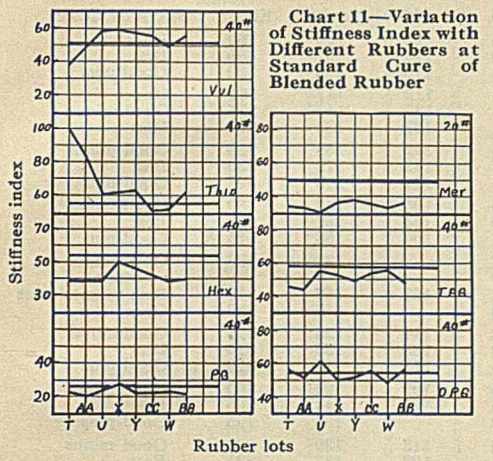


Chart 11—Variation of Stiffness Index with Different Rubbers at Standard Cure of Blended Rubber

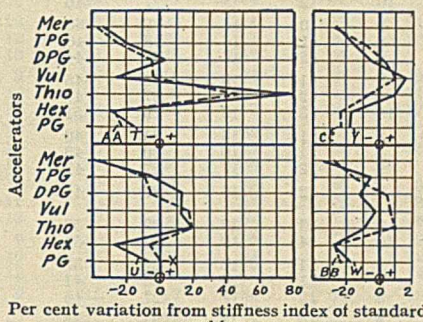


Chart 12—Effect of Accelerator on Change of Stiffness Index at Standard Cure of Blended Rubber

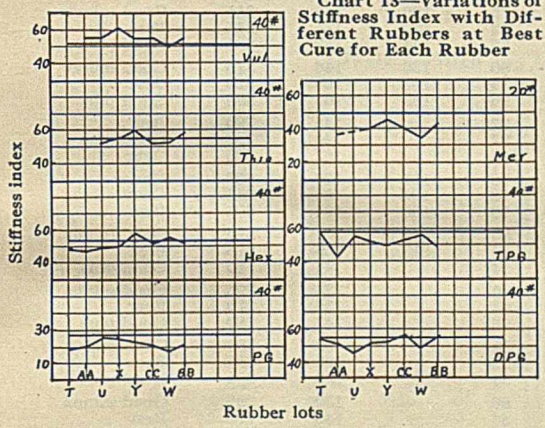


Chart 13—Variations of Stiffness Index with Different Rubbers at Best Cure for Each Rubber

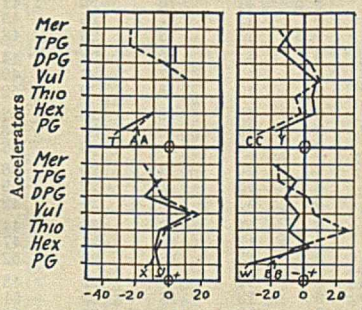


Chart 14—Effect of Accelerator on Change of Stiffness Index at Best Cure of Each Rubber

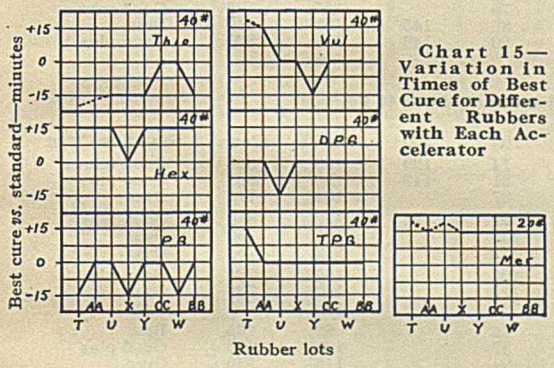


Chart 15—Variation in Times of Best Cure for Different Rubbers with Each Accelerator

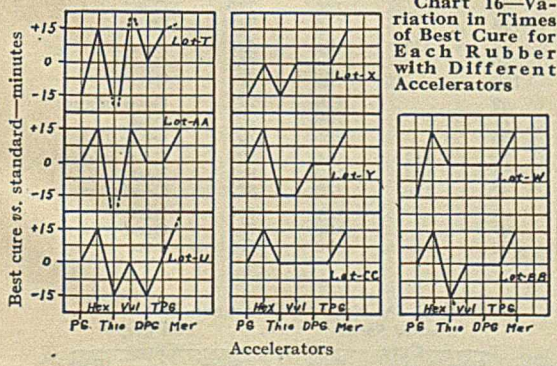


Chart 16—Variation in Times of Best Cure for Each Rubber with Different Accelerators

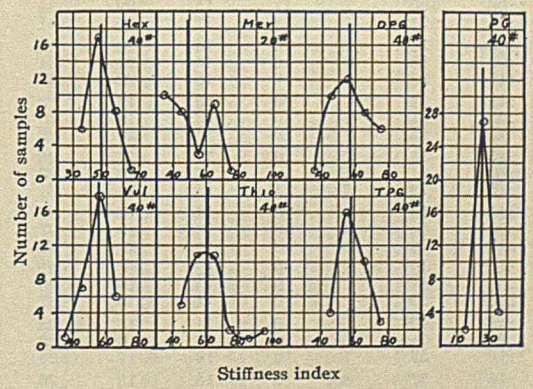


Chart 18—Distribution Curves for Accelerators

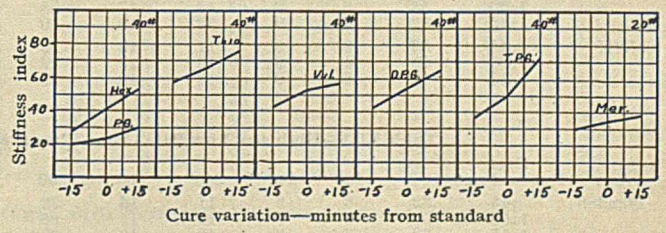


Chart 17—Average Increase of Stiffness Index with Cure

ceived in the rubber factories, is considerable for all types of mixings.

Distribution curves for the various types of mixings were intended to indicate the relative variability of different types of mixing with respect to the stiffness index at the standard cure. The number of tests upon which these curves were based, however, was too small to be considered more than an indication, particularly for pale crepe.

If the S. I.'s for all the lots of smoked sheets tested are averaged for each accelerator and compared with the S. I. for the blended rubber, it is found that there is close agreement at the best cure, except for pure gum. The same comparison for pale crepe shows similar results, mercapto being low as well as pure gum.

Possible Causes for Variation

It has been shown by many investigators that the by-substances in rubber vary considerably in the proportions in which they appear. It seems probable that most, if not all, of the variations experienced in vulcanization are due to the variation in these nonrubber constituents. We know, for instance, that rubber contains natural accelerators, resin acids, and natural tannin substances. It is known that stearic acid accelerates TPG, retards DPG, and has little or no effect on Vulcone. Since stearic acid behaves much like natural resin acids, we might expect similar effects from the resin acids. It is known that tannic acid accelerates mercapto and retards DPG, also that certain accelerators react to produce more than additive vulcanization effects, both in cure and quality. We further know that most ac-

Table VII—High and Low Smoked Sheets, Cured with Mercaptobenzothiazole at 20 Pounds

Lot	Cure Hrs. and min.	S. I.	100	200	300	400	500	600	700	800	Tensile	Elong.	State of Cure
Blended	:45	37	5	8	10	13	19	31	56	98	130	860	Under
	1:00	55	6	9	12	17	25	42	80	140	167	835	Best
	1:15	59	6	10	13	18	27	46	86	148	163	820	Good plus
HHH	:45	44	6	8	10	14	22	36	66	112	147	860	Under
	1:00	49	6	8	11	15	23	40	72	123	144	835	Good minus
	1:15	55	6	9	12	17	26	44	81	137	137	800	Best
A	:45	58	6	8	11	16	25	45	83	142	158	825	Good minus
	1:00	59	6	9	12	17	27	47	86	149	172	830	Best
	1:15	65	7	10	13	18	29	51	94	162	165	805	Good plus
KKK	:45	49	6	8	11	15	24	40	73	125	143	830	Good minus
	1:00	53	6	8	11	16	26	43	79	135	157	830	Best
	1:15	60	6	9	12	17	27	47	87	150	158	815	Good plus
MMM	:45	60	6	9	12	17	27	48	87		132	780	Good minus to best
	1:00	62	6	9	13	18	29	50	91	153	157	810	Best to good plus
	1:15	65	7	10	14	19	31	54	96		150	790	Over
LLL	:45	46	5	8	11	15	22	37	68	114	126	820	Good minus
	1:00	49	5	8	11	16	23	41	72	125	136	815	Best
	1:15	57	6	9	12	17	27	46	84	143	147	810	Good plus
GGG	:45	43	6	8	10	14	21	35	64	109	124	830	Good minus
	1:00	51	6	9	11	16	24	41	75	127	144	825	Best
	1:15	54	6	9	12	17	26	45	80		133	795	Good plus
RRR	:45	46	5	7	10	14	20	36	66	113	130	830	Good minus
	1:00	48	5	8	10	15	23	39	71	122	137	825	Best
	1:15	53	6	9	11	16	25	44	78		133	795	Good plus
SS	:45	52	6	8.5	11	16	23	41	75	130	165	855	Good minus
	1:00	57	7	9	12	17	25	45	82	142	175	845	Best
	1:15	61	7.5	9.5	13	18	28	48	89	154	182	835	Good plus
ZZ	:45	56	6	8	11	16	24	44	80	136	146	815	Good minus
	1:00	62	6	9	12	17	27	49	89	153	168	820	Best
	1:15	67	6	9	13	18	29	52	96	163	165	805	Good plus
XXX	:45	63	6	9	12	18	29	52	92		146	790	Best
	1:00	66	7	9	13	19	31	55	97		148	780	Good plus
	1:15	71	7	9	14	20	33	58	104		167	795	Over
YY	:45	46	5	7	10	14	20	36	66	111	126	825	Under
	1:00	50	5	8	11	15	22	39	72	125	154	845	Good minus
	1:15	52	6	9	11	16	24	42	76	133	134	805	Best
PPP	:45	55	5	8	11	16	25	44	80	136	141	810	Good minus
	1:00	58	5	8	12	17	26	47	84	143	159	825	Best
	1:15	63	6	9	13	18	30	52	93		144	785	Good plus
SSS	:45	59	6	9	12	17	27	48	86		138	795	Good minus
	1:00	64	6	9	13	18	29	51	93		135	770	Best
	1:15	65	6	9	13	19	31	53	96		147	780	Good plus
UUU	:45	50	6	8	11	15	24	40	74		98	760	Good minus
	1:00	53	6	8	11	16	25	42	78		126	785	Best
	1:15	55	6	8	11	17	26	44	81	132	136	805	Good plus
WWW	:45	54	6	9	11	16	26	45	80		130	795	Good minus
	1:00	58	6	9	12	17	28	49	86		140	795	Best
	1:15	62	6	9	13	19	30	52	92		144	785	Good plus
NNN	:45	53	6	8	11	16	25	43	78		125	795	Good minus
	1:00	59	6	9	12	17	27	48	86	145	152	810	Best
	1:15	61	6	9	13	18	29	50	90	146	146	800	Good plus

Table VIII—High and Low Pale Crepe, Cured with Thiocarbanilide at 40 Pounds

Lot	Cure Hrs. and min.	S. I.	100	200	300	400	500	600	700	800	Tensile	Elong.	State of Cure
Blended	:45	52	6	9	11	16	22	39	74	129	133	805	Good minus
	1:00	56	6	9	12	17	25	42	81	147	150	805	Good plus
	1:15	69	7	10	13	19	28	49	97		154	775	Over
T	:45	66	5	9	12	17	26	48	92	166	172	810	Good plus
	1:00	100	6	11	15	22	35	69	135		181	750	Over
	1:15	121	7	11	17	25	41	84	162		212	750	Over
AA	:45	78	6	10	14	20	28	54	106		156	765	Good plus
	1:00	83	7	10	15	21	31	58	114		142	735	Over
	1:15	93	7	10	15	22	31	62	124		168	750	Over
U	:45	52	7	10	13	17	23	39	75		92	735	Best
	1:00	61	7	10	13	18	26	44	87		130	765	Good plus
	1:15	65	7	10	14	20	29	49	94		118	735	Over
X	:45	55	7	10	13	17	25	43	80		133	780	Best
	1:00	61	7	11	15	20	29	47	90		126	770	Good plus
	1:15	72	7	11	15	21	31	53	103		113	715	Over
Y	:45	59	6	10	13	18	27	46	86	153	174	825	Best
	1:00	62	6	10	13	19	27	46	89		134	765	Good plus
	1:15	78	6	10	14	21	31	55	109		164	770	Over
CC	:45	48	7	9	12	16	21	37	69		110	775	Good minus
	1:00	52	7	10	13	18	25	40	77		128	785	Best
	1:15	59	7	10	14	19	27	44	86		158	795	Good plus
W	:45	49	5	9	11	15	22	37	71	127	144	825	Good minus
	1:00	51	6	9	12	16	22	37	73	134	162	835	Best
	1:15	57	7	10	13	17	25	51	82	150	172	825	Good plus
BB	:45	57	6	9	13	18	26	44	83		144	795	Best
	1:00	62	6	9	13	18	26	46	87		150	795	Good plus
	1:15	67	7	10	14	19	28	48	95		162	790	Over

celerators need zinc to produce the best quality, and require the presence of some acid to render the zinc soluble in the rubber. We may therefore assume that a variation in the acid content and natural accelerator content of the rubber would be quite likely to cause variation in the cure and quality of these rubbers, and the effects may well be different with different accelerators.

Table H—Average Acid Numbers

Accelerator	*Smoked Sheets* Cure Slow	Av.	Fast	*Pale Crepe* Cure Slow	Av.	Fast
Pure gum	247	220	193	...	254	232
Hex	...	240	204	250	244	...
Thio	...	240	204	247	253	241
Vul	234	220	201	241	247	271
DPG	241	233	194	...	251	233
TPG	289	212	...	...	249	...
Mer	269	214	199	226	256	...

Table IX—High and Low Pale Crepe, Cured with Triphenylguanidine at 40 Pounds

Lot	Cure Hrs. and min.	S. I.	100	200	300	400	500	600	700	800	Tensile	Elong.	State of Cure
Blended	:45	39	5	8	10	13	18	30	57	98	133	850	Under
	1:00	58	6	9	12	16	23	41	81		135	765	Best
	1:15	70	7	9	13	18	27	49	97		150	775	Good plus
T	:45	42	7	9	12	15	20	34	62	113	142	845	Under
	1:00	46	7	9	12	16	22	37	68	126	146	800	Good minus
	1:15	59	7	10	13	18	25	43	84		147	795	Best
AA	:45	33	5	7	9	12	16	26	49	90	130	870	Under
	1:00	44	5	8	10	14	20	33	64	118	162	860	Best
	1:15	70	6	9	13	18	26	47	96	173	176	800	Good plus
U	:45	38	5	7	10	12	17	29	55	101	135	855	Good minus
	1:00	55	5	7	11	15	21	39	76	139	154	820	Best
	1:15	84	6	10	14	20	30	58	114		170	770	Over
X	:45	36	5	7	9	12	17	28	53	99	128	850	Good minus
	1:00	53	5	8	11	15	20	37	73	133	142	815	Best
	1:15	75	6	9	13	19	28	52	103	184	199	815	Good plus
Y	:45	37	5	7	9	12	17	28	54	99	116	830	Good minus
	1:00	49	6	8	10	14	20	34	69	128	144	825	Best
	1:15	60	6	9	12	16	23	41	83	150	160	815	Good plus
CC	:45	38	5	7	9	12	17	30	55	100	137	860	Under
	1:00	53	5	8	11	15	21	37	74	135	168	845	Best
	1:15	82	6	9	13	18	26	53	108		176	780	Over
W	:45	37	4	7	9	12	17	28	54	100	132	855	Good minus
	1:00	55	5	8	11	15	22	39	77	144	164	825	Best
	1:15	71	6	9	12	17	26	48	97		166	790	Good plus
BB	:45	40	5	7	10	13	18	30	58	105	143	860	Under
	1:00	49	5	8	11	15	20	35	69		161	790	Best
	1:15	77	6	10	13	18	28	53	105		168	765	Good plus

Table X—High and Low Pale Crepe, Cured with Vulcone at 40 Pounds

Lot	Cure Hrs. and min.	S. I.	100	200	300	400	500	600	700	800	Tensile	Elong.	State of Cure
Blended	:45	42	5	8	10	13	19	32	61	107	114	810	Good minus
	1:00	51	6	9	11	14	21	37	72	130	140	815	Best
	1:15	53	6	9	11	15	22	39	75	136	145	815	Good plus
T	:45	32	5	7	9	12	17	27	49	90	130	875	Under
	1:00	37	6	8	10	13	18	30	55	99	140	875	Under
	1:15	40	7	8	11	15	20	33	60	110	142	850	Good minus
AA	:45	44	5	8	10	14	20	34	64	123	150	830	Under
	1:00	49	5	8	10	14	21	37	70	123	160	855	Good minus
	1:15	56	6	9	12	16	25	43	81		146	800	Best
U	:45	50	5	8	11	14	20	36	70	124	134	815	Good minus
	1:00	57	6	9	11	15	23	39	80	145	166	825	Best
	1:15	58	6	9	12	16	23	41	81	145	187	850	Good plus
X	:45	53	5	8	10	14	19	34	72	129	161	845	Good minus
	1:00	60	6	9	11	15	22	42	82	148	168	855	Best
	1:15	65	6	9	12	15	23	46	88	158	193	840	Good plus
Y	:45	55	5	8	11	15	23	41	78	141	161	825	Best
	1:00	59	6	9	12	16	23	42	82	146	167	825	Good plus
	1:15	63	7	10	13	18	26	47	89	160	160	800	Over
CC	:45	51	5	8	11	13	19	36	70	129	167	850	Good minus
	1:00	56	5	8	11	14	21	38	77	141	170	835	Best
	1:15	64	5	8	11	15	22	41	86	157	185	830	Good plus
W	:45	41	5	8	9	13	19	32	60	114	132	825	Good minus
	1:00	50	5	8	10	14	19	35	69	125	171	860	Best
	1:15	57	5	8	11	15	22	40	79	143	173	835	Good plus
BB	:45	49	5	8	11	15	21	36	70	125	140	820	Good minus
	1:00	54	6	9	12	16	22	39	76	137	172	815	Best
	1:15	55	7	9	12	16	23	41	78	142	158	820	Good plus

Table XI—High and Low Pale Crepe, Cured with Hexamethylenetetramine, at 40 pounds

Lot	Cure Hrs. and min.	S. I.	100	200	300	400	500	600	700	800	Tensile	Elong.	State of Cure
Blended	:45	36	5	7	9	11	16	27	52	89	137	870	Under
	1:00	54	5	8	11	14	21	38	75	137	150	820	Best
	1:15	75	6	9	12	17	28	48	102	174	179	800	Over
T	:45	23	5	6	8	10	14	21	37	67	115	900	Under
	1:00	38	6	7	11	15	18	30	56	105	134	845	Good minus
	1:15	48	6	8	11	16	20	36	58	123	146	830	Best
AA	:45	32	5	6	8	10	13	20	62	62	98	890	Under
	1:00	39	6	7	10	13	18	31	57	103	123	835	Good minus
	1:15	48	6	8	11	15	20	35	68	125	138	820	Best
U	:45	25	5	8	9	11	13	21	38	70	126	905	Under
	1:00	39	5	8	9	12	16	28	55	102	126	840	Good minus
	1:15	49	6	8	11	13	20	35	69	129	168	845	Best
X	:45	32	5	7	10	12	16	26	48	87	120	860	Under
	1:00	50	6	9	11	15	21	37	71	127	174	860	Best
	1:15	60	6	9	12	17	24	43	84	152	152	800	Good plus
Y	:45	26	5	8	10	13	16	24	42	75	118	885	Under
	1:00	45	7	9	12	15	21	35	66	119	146	835	Good minus
	1:15	57	8	10	13	17	25	43	82	150	168	825	Best
CC	:45	30	5	6	8	10	13	22	43	80	120	875	Under
	1:00	42	5	8	10	13	18	31	60	115	156	855	Good minus
	1:15	53	5	9	11	15	21	37	74	140	160	825	Best
W	:45	26	5	7	9	11	15	34	41	76	114	880	Under
	1:00	39	6	8	11	14	18	30	57	104	154	880	Good minus
	1:15	56	6	9	12	15	22	39	78	143	164	825	Best
BB	:45	27	5	8	9	11	15	23	42	79	142	910	Under
	1:00	39	6	9	10	13	17	29	56	106	164	880	Good minus
	1:15	52	6	9	11	14	20	36	72	138	176	845	Best

It may be of interest to note that pigments having active surfaces, such as zinc oxide and carbon black, and therefore capable of adsorbing certain ingredients in rubber, may, when the amounts of these ingredients are small, exert a profound effect upon the cure, although when larger amounts of the ingredients are present the effect may be negligible.

Table H shows average acid numbers for slow, average, and fast curing rubbers in the different types of mixing.

Future Work

Results of this investigation lead inevitably to the conclusion that mere compounding investigation will be in-

Table XII—High and Low Pale Crepe, Cured with Diphenylguanidine at 40 Pounds

Lot	Cure Hrs. and min.	S. I.	100	200	300	400	500	600	700	800	Tensile	Elong.	State of Cure
Blended	:45	41	5	7	10	13	17	30	58	115	140	855	Good minus
	1:00	54	6	8	11	15	21	38	75	141	167	840	Best
	1:15	64	6	9	12	17	25	44	89	159	162	810	Good plus
T	:45	40	6	8	10	13	17	29	57	108	162	870	Good minus
	1:00	55	6	9	12	15	21	37	76	143	178	840	Best
	1:15	69	6	9	13	17	25	46	94	178	181	805	Over
AA	:45	40	5	7	10	13	17	30	57	107	120	825	Under
	1:00	52	6	8	12	15	21	38	73	133	168	845	Best
	1:15	65	6	9	13	18	25	46	90	165	177	815	Good plus
U	:45	46	5	8	11	13	18	31	64	118	158	855	Good minus
	1:00	61	5	8	11	16	23	42	84	154	206	855	Good plus
	1:15	76	7	10	13	18	27	50	103	180	200	810	Over
X	:45	36	5	8	9	12	17	28	53	85	144	875	Under
	1:00	51	6	9	11	15	21	37	72	117	154	820	Best
	1:15	57	6	9	12	16	23	46	80	133	156	810	Good plus
Y	:45	45	6	8	11	14	19	33	64	117	153	850	Good minus
	1:00	52	6	9	12	15	22	38	74	137	147	815	Best
	1:15	64	6	9	13	17	26	46	90	165	180	815	Over
CC	:45	46	5	8	10	13	18	32	64	120	176	870	Good minus
	1:00	55	5	9	11	15	21	37	76	143	171	830	Best
	1:15	67	5	9	12	17	25	45	92		164	795	Over
W	:45	37	6	7	9.5	12	16	29	53	98	150	885	Good minus
	1:00	48	6	8	10	14	19	34	67	125	186	855	Best
	1:15	64	6	9	12	16.5	23	43	87	161	166	805	Good plus
BB	:45	47	6	9	11	14	19	33	66		119	790	Good minus
	1:00	55	6	9	12	16	21	38	76	139	154	820	Best
	1:15	68	8	11	14	18	25	46	93	176	176	800	Good plus

Table XIII—High and Low Pale Crepe, Cured with Mercaptobenzothiazole at 20 Pounds

Lot	Cure Hrs. and min.	S. I.	100	200	300	400	500	600	700	800	Tensile	Elong.	State of Cure
Blended	:45	34	5	8	10	12	16	27	50	90	137	885	Under
	1:00	49	6	9	11	15	22	38	71	127	129	805	Best
	1:15	58	7	9	12	17	24	44	82	145	172	835	Good plus
T	:45	26	4	6	8	11	15	24	41	74	120	890	Under
	1:00	33	5	7	9	13	17	26	50	89	127	870	Good minus
	1:15	35	6	8	10	14	19	29	54	98	130	850	Good minus
AA	:45	28	5	6	8	11	14	24	42	75	125	900	Under
	1:00	31	5	6	9	12	17	30	48	87	132	875	Good minus
	1:15	37	6	7	10	14	19	31	56	101	103	810	Best
U	:45	23	5	6	8	11	14	21	37	67	112	900	Under
	1:00	30	5	7	9	12	16	26	46	83	118	865	Under
	1:15	32	6	7	10	13	18	28	50	93	138	875	Good minus
X	:45	31	5	7	9	12	17	26	48	84	132	885	Under
	1:00	36	6	8	10	13	19	30	55	99	154	885	Good minus
	1:15	41	6	9	11	15	21	34	62	111	150	860	Best
Y	:45	33	5	7	9	12	17	27	50	89	150	900	Under
	1:00	37	5	7	10	13	19	30	56	102	156	880	Good minus
	1:15	45	6	8	11	15	21	34	66	118	150	845	Best
CC	:45	33	5	7	9	12	17	28	50	90	108	835	Under
	1:00	36	5	8	10	13	19	30	55		83	770	Good minus
	1:15	41	6	9	11	14	21	33	62	112	114	805	Best
W	:45	28	5	7	9	12	16	25	44	78	78	800	Under
	1:00	33	6	8	10	13	17	28	50	87	92	810	Good minus
	1:15	35	6	8	11	14	19	30	54		92	795	Best
BB	:45	35	5	7	9	12	17	28	50	90	134	875	Under
	1:00	36	5	8	10	13	18	29	54	97	146	875	Good minus
	1:15	41	6	9	11	14	20	32	61	109	114	810	Best

Table XIV—High and Low Pale Crepe, Cured with Pure Gum at 40 Pounds

Lot	Cure Hrs. and min.	S. I.	100	200	200	400	500	600	700	800	900	Tensile	Elong.	State of Cure
Blended	2:00	22	4	7	8	10	12	16	23	38	69	97	965	Under
	2:15	27	5	7	9	11	13	18	26	45	87	112	945	Good minus
	2:30	34	5	7	10	12	15	20	30	54	104	112	915	Good plus
T	2:00	19	4	6	8	10	13	15	20	34	65	102	980	Best
	2:15	23	5	7	9	11	13	17	23	40	77	116	970	Over
	2:30	35	5	8	10	12	16	21	31	56	109	134	940	Over
AA	2:00	19	4	6	8	9	12	14	20	33	62	80	945	Good minus
	2:15	21	4	6	8	9	13	15	21	36	69	100	965	Best
	2:30	28	5	7	9	11	15	19	27	47	90	107	945	Over
U	2:00	22	5	7	8	10	12	15	22	37	67	102	975	Good minus
	2:15	25	5	7	8	11	13	17	23	42	79	118	970	Best
	2:30	31	5	7	9	12	15	19	27	50	95	126	950	Over
X	2:00	24	6	7	9	11	13	16	23	40	72	76	910	Best
	2:15	27	6	7	9	11	15	18	26	45	82	106	945	Over
	2:30	32	6	8	10	12	17	21	29	53	100	128	940	Over
Y	2:00	21	5	7	9	10	12	15	21	36	67	108	985	Good minus
	2:15	22	5	7	9	11	13	17	23	39	76	115	970	Best
	2:30	32	6	8	10	12	16	21	30	53	102	114	930	Over
CC	2:00	17	4	6	8	9	11	14	19	31	57	81	960	Good minus
	2:15	21	5	7	9	10	13	16	22	37	99	109	970	Best
	2:30	30	5	7	9	12	15	19	28	49	121	130	965	Over
W	2:00	18	5	7	8	10	12	16	21	34	61	93	980	Best
	2:15	22	5	7	8	10	13	17	23	38	70	102	965	Good plus
	2:30	28	6	8	9	12	15	20	28	48	91	123	955	Over
BB	2:00	17	4	5	7	9	11	13	18	30	55	70	955	Under
	2:15	21	5	6	8	10	13	16	21	37	68	80	930	Best
	2:30	24	5	7	8	11	14	17	24	41	80	102	950	Over

sufficient to disclose the causes for rubber variation. It will be necessary to isolate the materials that are influencing cure and quality, and determine their effects upon each other and upon commonly used accelerators, before we can hope to place ourselves in a position to counteract these variables and to pass the word along to the rubber growers, telling them which variables they must control.

Conclusions

1—It is insufficient to use one, or even two or three, mixings to evaluate rubber for use with miscellaneous accelerators.

2—Adjustment of cure is the most important problem.

3—Variation in quality exclusive of cure is of real importance.

4—S. I. at best cure gives a better idea of quality changes than slope, tensile, ultimate elongation, tensile product, energy of resilience, or coefficient of vulcanization.

5—Tear resistance is an important property, particularly as a criterion for cure.

6—In order to specify rubber quality it will be necessary to specify the mixing used, until such time as the causes of variation are understood and means provided for eliminating or counteracting them.

Table XV—Stiffness Index *vs.* Slope in Pure Gum at 40 Pounds

Smoked Sheets					*Pale Crepe*				
Rubber lots	Slope 200	Slope 215	Slope 230	S. I. (best cure)	Rubber lots	Slope 200	Slope 215	Slope 230	S. I. (best cure)
3R	40	*38*	38	42	T	*44*	38	36	19
2S	*36*	36	34	56	AA	38	*36*	34	21
3X	*36*	36	36	53	U	39	*36*	34	25
3H	42	38	*36*	46	X	*38*	34	32	24
3K	42	40	*34*	38	Y	38	*38*	34	21
3M	36	*34*	34	56	CC	38	*38*	36	21
3L	40	42	*38*	44	W	*38*	36	36	18
3G	34	36	*38*	43	BB	40	*40*	36	21
1A	35	*36*	34	40					
2Z	38	*38*	36	46					
2Y	40	*34*	34	42					
3P	*38*	38	38	49					
3S	*36*	34	36	53					
3U	*38*	36	36	65					
3W	*40*	36	38	52					
3N	*36*	36	38	50					

The Settling and Packing of Mixed Paints[1]

By William C. Arsem

226 State St., Schenectady, N. Y.

In a mixed paint the pigment grains are to some extent deflocculated and dispersed by the free acids in the vehicle, and the metallic soaps are maintained in the sol condition by the same agency. If no chemical changes take place in this system, the pigment grains may settle through the action of gravity, but will not adhere, and soft settling will result.

In a stored paint slow chemical reaction between basic pigments and free acids forms basic soaps with little dispersing power. Some of the soap will be precipitated as a result of this loss of free acid from the vehicle, and the pigment grains which are thus freed from adsorbed dispersing agent tend to adhere to each other by virtue of the free surface valences. When the removal of dispersing agent occurs after gravity has done its work in bringing the particles close together, they will adhere more or less strongly to each other and hard settling will be the result.

IT HAS long been known that paints in storage undergo changes which cause the pigment to settle to the bottom of the can, forming a dense layer which is not easily incorporated with the supernatant liquid by working and stirring. In the past it appears that a purely chemical explanation has been sought for the phenomenon of packing in storage.

Gardner[2] has indicated that oils alone and in contact with pigments may undergo hydrolysis in presence of moisture. Ware and Christman[3] have discussed the action of rosin and fatty acids on zinc oxide. They think that water and other substances added to paint as emulsifying agents hydrolyze the oil, and that the fatty acids form insoluble zinc and lead soaps, which, if free to precipitate, form a skin. They show that a naphtha solution of rosin dissolves zinc oxide to a clear solution and also dissolves the skin which forms on paint, and they attribute the latter action to the formation of a soluble zinc resinate. Gardner[4] has also again pointed out that basic pigments can react with fatty acids and resins in the paint vehicle to form soaps that are insoluble in naphtha but soluble to some extent in the presence of free fatty or resin acids.

The Nature of Paint

Paint is a heterogeneous mixture of solids and liquids in which the phenomena of adsorption and peptization are very important. It offers a fertile field for the study of surface chemistry. The pigments have individual characteristics, and the liquids are often extremely complex. In order to direct attention to these factors, the ingredients of paints will be discussed in some detail.

It may be well to define the terms used in this paper, because they are used by various workers in this field in a sense somewhat different from their significance in other fields.

Adsorption is used to mean an unequal distribution of a substance between two phases of a heterogeneous mixture. As applied to paint, we speak of the adsorption of a substance from the vehicle by the pigment, having in mind a condition in which the free surface of the pigment is more or less completely covered over with molecules of the adsorbed substance, which are thus closer together or in greater concentration than they are in the vehicle. The mechanism of adsorption, according to the latest views,[5] involves an attraction of the molecules of adsorbed substance by residual valences at the surface of a space lattice, so that we may conceive the molecules of adsorbed substance as being attached to the surface of the pigment grains in an oriented relation to the surface.

Dispersion is the normal result of adsorption and peptization and should mean no more than a separation of the particles of the dispersed phase from each other. The mechanism by which this occurs is by no means clear, but the following explanation is offered without proof at this time:

Owing to the mutual solubility relations of the dispersing agent and the solvent, the dispersing agent is probably not completely withdrawn from the solvent as a result of the adsorption process, leaving a sharp surface of demarcation; but we may conceive that each particle of pigment with the adsorbed molecules of dispersing agent always has an atmosphere of solvent which is bound or attached to the hydrocarbon chains of the dispersing agent by weak valence forces of the same kind as those concerned in ordinary solution processes.

This leads to a conception of a definite structure for the interface between a dispersed solid phase and the liquid continuous phase. From a thermodynamic standpoint this view is admissible, as indicated by the following excerpt from a standard textbook:[6]

> The boundary between two contiguous phases, which is known as a surface or an interface, is not a mathematical boundary of only two-dimensional extension. There is a minute though finite region in which the prop-

[1] Presented before the Section of Paint and Varnish Chemistry at the 69th Meeting of the American Chemical Society, Baltimore, Md., April 6 to 10, 1925.

[2] *J. Franklin Inst.*, **177**, 533 (1914).

[3] *Trans. Am. Inst. Chem. Eng.*, **9**, 115 (1917).

[4] *Paint Mfrs'. Assoc. U. S., Tech. Circ.* **143** (1922).

[5] Langmuir, *J. Am. Chem. Soc.*, **38**, 2221 (1916).

[6] Lewis and Randall, "Thermodynamics," 1st ed., p. 247.

erties differ appreciably from the properties in the interior of either phase, and vary from point to point.

According to this view, we may recognize theoretically different degrees of dispersion of the pigment, depending on what proportion of the atomic spaces on the total surface of all the pigment grains is occupied by adsorbed molecules of dispersing agent, and what proportion of the solvent is bound by the solubility relations between it and the dispersing agent. In practice, the smoothness, flow, and stability of a paint would depend on these factors.

Peptization is a special and extreme case of dispersion through which the dispersed phase is in very small particles or aggregates of a few molecules, so that each system, consisting of a small solid (or liquid) aggregate surrounded by molecules of adsorbed substance, is small enough to remain permanently suspended in the surrounding liquid phase.

Flocculation. In a system containing a peptized substance, the removal of some of the peptizing agent in any way tends to uncover some of the adsorbing surface of the peptized particles, and the active valences on these exposed surfaces tend to attract each other so that certain of the particles coalesce and the free surface is eliminated. This is what is meant by flocculation in the case of a fully peptized solid phase in a sol, and in this case some of the solid phase will be precipitated. As applied to systems in which the dispersed particles are all of relatively large dimensions, as in a paint, flocculation causes adherence of adjacent pigment grains and loss of fluidity, although there is no coalescence to form large, continuous aggregates. The particles, although having some attraction for each other, do not adhere strongly together, but behave as though there were no lubrication at the points of contact.

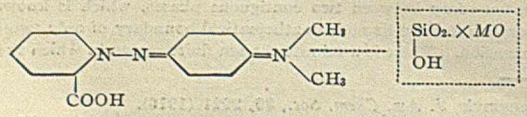
When a pigment is placed in a vehicle containing nothing that can be adsorbed by it, the particles of pigment tend to adhere to each other or to flocculate. If the aggregates are broken up mechanically they will tend to reform. A mixture like this would not make a good paint because it would lack easy flow, although on standing the pigment probably would not settle into a hard, compact mass. If a free acid is present, however, particularly if the pigment is strongly basic, the dispersing agent is adsorbed on the surface of the pigment grains, and they thereupon become dispersed throughout the liquid and the mixture assumes more or less the character of paint. As long as nothing happens to disturb this arrangement, coalescence should not take place and the paint should remain soft and free-flowing, although the pigment may settle more or less, particularly if the amount of dispersing agent is small.

Pigments

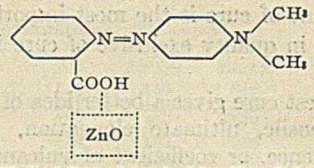
Any solid substance has at the surface unbalanced valences which are manifested as power to adsorb certain classes of substances.

Pigments may be classified as acid or basic by their behavior toward solutions of dyes, and more particularly by means of amphoteric indicators such as methyl red. Asbestine, for instance, adsorbs the color from a water solution of a basic dye such as fuchsine or methyl violet. It will also become pink when placed in a pale yellow solution of neutral methyl red in naphtha. This behavior must mean that asbestine adsorbs methyl red in such a way that it is attached at the basic end of the molecule, which then changes its configuration and becomes red just as it does in the presence of strong mineral acids. We may then class asbestine as an acid pigment.

Pure zinc oxide in a neutral methyl red solution becomes yellow, so that the indicator molecule must be attached to the zinc oxide surface by its carboxyl group.



Methyl Red, Adsorbed by Asbestine



Methyl Red, Adsorbed by Zinc Oxide

Composite pigments, such as lithopone and leaded zinc oxide, appear to be self-compensated by mutual adsorption of their constituents, and do not react clearly toward methyl red. The test with methyl red in naphtha is an extremely sensitive one for detecting acid impurities in basic pigments. Commercial white lead and zinc oxide show small pink specks, and commercial whiting becomes entirely pink owing to the presence of silica, while precipitated chalk gives a pure yellow color.

Some common substances, including pigments, are classified thus by the methyl red test:

Acid	Basic	Neutral or Doubtful
Kieselguhr	Zinc oxide	Leaded zinc oxide
Tripoli	White lead	
Talc		
Serpentine asbestos		
Amphibole asbestos		
Barytes		
Gypsum		

The classification of a solid as "acid" does not mean that it will not adsorb acid substances at all, because it is conceivable that the surface of a solid lattice will exhibit both positive and negative valences. In fact, it can be shown that even acid pigments will adsorb fatty acids to some extent.

Vehicles

A paint vehicle contains:

Drying oils—linseed, China wood, soy bean, etc.
Free fatty acids
Acid anhydrides
Free resin acids
Resins
Metallic soaps

Treated oils may be partly polymerized, or partly oxidized, or both. In any case there will be present molecular aggregates of two or more units, and also some free acid resulting from chemical changes taking place in the process. A sol condition often results in which the glyceride aggregates are peptized by the free acid.

Free fatty acids may come from the original oil or may be produced by treatment as just stated.

Free resin acids may come from any of the resinous ingredients.

The resins may include ordinary rosin, rosin ester gum, or any of the commercial varnish gums.

The metallic soaps include the resinates, linoleates, tungates, and other fatty acid and unsaturated acid salts of calcium, lead, manganese, cobalt, and zinc. These metallic soaps are as a rule not soluble in naphtha but will form sols under particular conditions. Zinc oleate, made by dissolving zinc oxide in the equivalent weight of hot oleic acid, is easily dispersed in naphtha, when freshly prepared, but the sol goes over into a gel within a few hours. The same zinc oleate when 24 hours old will no longer disperse of itself into naphtha. Evidently the fresh soap is an unstable sol, which slowly changes into a gel, thus behaving like a gelatin sol which passes into a gel on standing.

A soap can form a sol in the presence of free fatty acid which appears to be adsorbed on the surfaces of the small molecular aggregates so as to prevent their coalescence into a gel. The stability of a soap sol depends on the concentration of the fatty acid in the solution, so that a stable sol may,

on dilution, become cloudy by precipitation of flocks of gel, although in some cases considerable time is required for the change.

It appears that there is a distribution of the peptizing agent between the solvent and the dispersed soap. To investigate this relation a certain obsolete type of factory liquid containing lead resinate and free acid was diluted with different amounts of naphtha, oleic acid being added in each case to just prevent precipitation, as shown by a faint opalescence. The relations between the concentration of acid and of lead resinate are shown in Figure 1.

The smaller the amount of soap present the more acid is required to keep it peptized. The relation is:

$$A = 1.75\,L^{-0.428}$$

This is a modification of the well-known Freundlich adsorption equation:

$$\frac{y}{m} = \alpha c^{\frac{1}{n}}$$

m = mass of adsorbing substance (in this case the dispersed phase)
y = mass of adsorbed substances (in this case the dispersing agent)
c = concentration of adsorbed substance in this solution at equilibrium

In the case of a sol the dispersed substance is uniformly distributed in very small aggregates, to which the adsorbed substance, or dispersing agent, is attached by active groups. However, the greater part of the molecule of the dispersing agent remains virtually in solution, hence c may be taken as the total concentration of dispersing agent at the critical point. Hence by making $y = c$, the equation becomes

$$c = \alpha m^{\frac{n}{n-1}}$$

or using A and L, as in Figure 1, we have

$$A = \alpha L^{\frac{n}{n-1}}$$

The explanation is that the additional solvent withdraws some of the peptizing agent from the surfaces of the units of the dispersed phase, and these free surfaces then coalesce to form larger aggregates, and these, if large enough, form a precipitate.

In the case of gloss oil a similar instability on dilution is observed, but the separation is very slow, requiring several days. A typical gloss oil may contain amounts of the several ingredients, which may be calculated as

	Per cent
Normal calcium resinate (or abietate)	37
Free rosin	25
Naphtha	38

When some of this was diluted to 25 per cent by adding more naphtha, and allowed to stand several days, the washed and fused precipitate contained 3.37 per cent ash. Normal calcium abietate $Ca(C_{19}H_{27}O_2)_2$ should yield 9.13 per cent ash. If one molecule of the normal soap were associated with two molecules of abietic anhydride, the chief constituent of rosin, as an acid soap or as an adsorption complex, the ash would be 3.24 per cent, a value very close to that found.

An alternative explanation for the precipitation of gloss oil on dilution is that rosin itself in the fused or freshly dissolved condition is a sol which is stabilized by calcium resinate in concentrated solutions, but slowly separates from dilute solutions. It is known from other experiments that rosin separates in crystalline form from solutions in kerosene or transformer oil, and it is also known that calcium resinate is a good stabilizer for heavy metal soap sols.

Certain blown oils contain constituents that are soluble in the balance of the oil, but when a thinner is added two immiscible liquid phases are produced, one high in the oxidized constituent and the other low.

Dispersion of Pigments in Vehicles

The particles of pigment tend to adhere to each other by virtue of the external unbalanced valences which tend to unite the lattices of solid particles at their points of contact. When a pigment is placed in a liquid, the particles will come together or flocculate unless the surface attraction is neutralized in some way. If a peptizing or dispersing agent is present the surface of the pigment particles adsorbs this substance so that every free valence at the surface of the pigment tends to satisfy itself by attaching an equivalent of dispersing agent. Since we now think of adsorption as a polar phenomenon (Langmuir, Harkins), we may consider, in the case of a basic pigment which has adsorbed a fatty

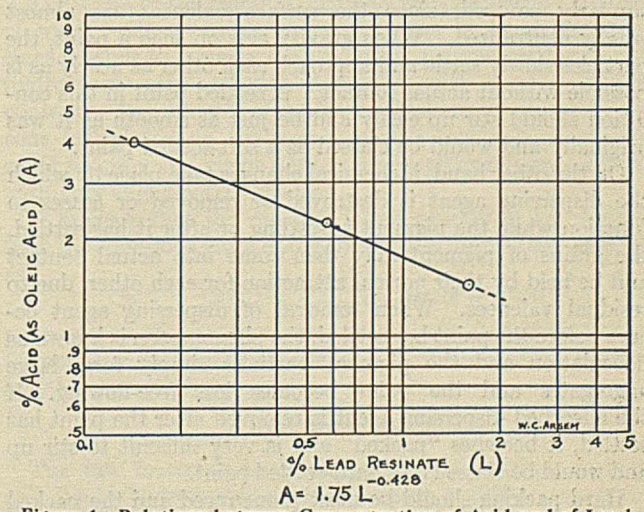


Figure 1—Relations between Concentration of Acid and of Lead Resinate

acid, that the molecules of acid are all oriented so that the carboxyl groups are attached to the surface of the solid particle while the hydrocarbon chains extend outward perpendicular to the surface.

Basic Soaps

By treating fatty acids dissolved in oils, and also oils with known acid content, with more than one equivalent of base such as white lead or basic zinc carbonate, basic soaps are obtained which as a rule are more soluble or more easily dispersed than the neutral or acid soaps. Basic zinc oleate has the formula $Zn(C_{18}H_{33}O_2)_2.Zn(OH)_2$.

When an oil containing free acid, such as bodied linseed oil, is treated at 200° to 250° C. with basic zinc carbonate, $2ZnCO_3.3Zn(OH)_2$, as much as eight equivalents of zinc to one of the acid may be introduced, but when more than two equivalents have been added the neutral glyceride begins to be broken down, as is shown by the increase in apparent acid value. (It should be noted that most soaps except those of calcium, when tested for acid value by the usual method, react as free acids, because the bases set free by the standard alkali do not react alkaline to phenolphthalein.[7]) These basic soaps in most cases do not disperse pigments, and are only weakly adsorbed, although basic lead soaps do disperse zinc oxide somewhat.

Slow Changes in Paints

"Soft-settling" and "hard-settling" are terms used to describe conditions in stored paints. When a paint is allowed to stand, the particles of pigment immediately begin to settle

[7] Ware and Christman, This Journal, 8, 996 (1916).

at a rate depending on their average size; and if the liquid contains no dispersing agent and the pigment particles consequently have no adsorbed layers, and, moreover, if they have no attraction for each other, they should settle freely and should eventually form a layer on the bottom in which the solid particles are closely packed together. If the particles are spherical and all of the same size, they should form a hexagonal, close-packed arrangement in which the solid particles occupy 74.04 per cent of the volume of the settled layer and the liquid between the solid particles occupies 25.96 per cent. In an actual paint, however, these hypothetical conditions do not exist. In the first place, each pigment particle is covered with an adsorbed layer of dispersing agent, which prevents adhesion of adjacent particles. On the other hand, each pigment particle with its adsorbed layer of dispersing agent is to a large extent rendered incapable of attracting a neighboring particle of pigment similarly covered, since the surface valences are almost wholly neutralized. When gravity acts on such a paint, the particles slowly settle and approach each other as nearly as is possible without actual contact. A settled paint in this condition should stir up easily and be just as smooth as it was originally and would be classed as a soft-settled paint.

On the other hand, if chemical changes take place by which the dispersing agent is destroyed or removed or ceases to function while the pigment is settling or after it has settled, the grains of pigment may then come into actual contact and be held by their normal attraction for each other, due to residual valences. When removal of dispersing agent occurs before the paint has settled, the phenomenon is known as flocculation and the pigment particles simply form large aggregates and the paint becomes less free-flowing. If the adsorbed dispersing agent is removed after the paint has settled, it becomes "packed" and is very difficult to stir up and would be classed as a hard-settled paint.

Hard packing should be most pronounced and the packed pigment should be most dense when just enough dispersing agent is present to separate all the individual particles so that settling shall be as free as possible and the pigment layer shall occupy a minimum apparent volume. Thus, a paint which is well ground and contains a plentiful amount of acid or resinous dispersing agents and to all appearance behaves like a good paint when freshly prepared may be much more likely to get into a condition favoring hard packing if the complex systems formed are unstable and the pigment can eventually lose its adsorbed layer.

We have now to show how the removal of dispersing agent and the change in the degree of deflocculation of the pigment can occur. In a paint the partly deflocculated pigment and the metallic soap sol in the vehicle, both stabilized by the same free acid, form a highly sensitive system. As soon as a pigment is ground with a vehicle chemical and physical changes begin to take place.

First, the pigment adsorbs fatty acid and possibly other substances from the vehicle. At this stage the paint consists of two unstable complex phases, one liquid and the other solid. The liquid phase has lost some of the dispersing agents which have previously stabilized the heavy metal soaps in the sol condition in the vehicle, so that the sols tend to revert more or less rapidly to the gel condition. As this change takes place the soaps may precipitate in a flocculent condition between the pigment grains as a blanket above the pigment or as a jelly or "pudding" throughout the entire mass of the paint.

The solid phase, consisting of pigment grains with adsorbed fatty acid on their surfaces, is chemically unstable if there is any possibility of a reaction between the pigment and the dispersing agent. If the pigment is basic and the dispersing agent is acid, a slow reaction will take place, forming a metallic soap. If the action between the basic pigment and the acid were to stop at the point at which a neutral soap is formed this neutral soap might also act as a dispersing agent, but it has been shown that the basic pigment, if it is white lead or zinc oxide, will continue to act on the neutral soap until a basic soap is formed and this basic soap has very little dispersing action on a pigment derived from the same metal.

We see, therefore, that as soon as the paint is once mixed unstable conditions immediately exist, and the inevitable changes toward chemical equilibrium tend to cause a loss of the characteristic properties of paint.

Chemical Changes in Stored Paints

Paints stored in cans were examined periodically for 22 months and determinations were made of acid value and ash content of the vehicle.

The acid value is a measure, not only of the free acid, but of the metallic soaps. In all cases the acid value decreased slightly with time, which was interpreted to mean a transition of a portion of the "drier" soaps from the sol to the flocculated or gel condition. The ratio of ash to total acid calculated as oleic acid was found to approach a constant value not far from 0.287, which is the ratio of zinc oxide to oleic acid in basic zinc oleate, $Zn(C_{18}H_{33}O_2)_2.Zn(OH)_2$, and zinc oxide was found in the ash of the vehicle.

It is considered highly probable that the zinc oxide in the paint slowly dissolves in the free acid, the normal end condition being that a soluble basic zinc soap is formed and all the acid neutralized. If there is no interference with the progress of this action, the ratio of the final ash content to the total combined and free acid should be 0.287 and the liquid should contain negligible amounts of the soaps of other metals which are thrown out when the liquid passes from the acid to the neutral condition. The vehicle in a stored paint thus finally loses most of its power to disperse pigments because of the loss of free acid and neutral soaps and the formation of basic soaps.

Acknowledgment

Acknowledgment is due to the Lowe Brothers Company, of Dayton, Ohio, for permission to publish this paper, and to D. A. Kohr, vice president, and to members of the staff for their coöperation and interest.

U. S. Gains Patent and Trade-Mark Relief

Very material relief from former onerous conditions affecting American patent rights in foreign countries resulted from the International Convention for the Protection of Industrial Property held at The Hague from October 8 to November 6, at which thirty-two countries were represented, according to Commissioner of Patents Thomas E. Robertson, chairman of the American delegation.

Practical elimination of the risk of forfeiture of a patent for nonworking or for nonpayment of taxes through accidental causes is described by the patent commissioner as one of the changes of outstanding importance.

An agreement was reached that the period of three years, which must be allowed before any penalty can be imposed for nonworking, is to be reckoned from the date of the grant of the patent instead of the filing of the application.

Another important development is the provision as to the cancellation of fraudulently registered trade-marks, furnishing "an effective remedy against piracy of well-known trade-marks." The amendments with relation to unfair competition will be of benefit, especially in those countries which have not developed, as have the United States and Great Britain, a well-defined system of jurisprudence with respect to unfair competition.

While in Commissioner Robertson's opinion the conference did not go so far on working patents and taxes thereon as the United States delegates proposed, the adoption of the present convention represents a long step forward in the direction of doing away entirely with requirements of working in order to maintain a patent in force and very materially diminishes the risk of a patentee losing his rights as in former years.

Calcium Cyanide—"Powdered Hydrocyanic Acid"[1,2]

A New Product of Manufacture

By F. J. Metzger

Air Reduction Co., Inc., New York, N. Y.

UP TO the present date no account has been published reporting calcium cyanide as recovered by evaporation or otherwise, on account of its ready decomposition due to hydrolysis or polymerization.

Prior work along these lines may perhaps best be summarized by quoting the following relevant excerpts from "The Chemistry of Cyanogen Compounds and Their Manufacture and Estimation," by Herbert E. Williams:

> Calcium Cyanide is known only in solution. * * *
> A solution of the salt may be readily prepared by passing hydrocyanic acid into milk of lime and a solution may be thus obtained of 30 to 35 per cent calcium cyanide, but such a solution is exceedingly unstable; it smells strongly of hydrocyanic acid, and cannot be kept unchanged for more than an hour or so. The solution quickly turning brown, and depositing dark brown flocks of azulmic acid and crystals of a sparingly soluble basic cyanide of calcium * *
> A solution of 15 per cent or under of calcium cyanide may be kept if out of air contact for years without change, but a solution of any strength above this figure will rapidly turn brown and decompose in the manner described, the rate of decomposition depending directly on the strength; the stronger the solution the quicker the decomposition. A solution of 20 per cent strength may be kept for a day without discoloration, while a 30 per cent solution turns brown in a few hours * * *
> Calcium cyanide does not appear to exist in the dry state, it cannot be obtained by evaporation and crystallization of the aqueous solution * * *

and from Thorpe's "Dictionary of Applied Chemistry," Vol. II (last edition):

> Calcium Cyanide has never been prepared in the pure state. An aqueous solution of lime in hydrocyanic acid decomposes completely into its constituents when boiled (Scheele). By evaporating such a solution *in vacuo*, Joannis obtained a crystalline compound, $3CaO.Ca(CN)_2$, $15H_2O$, which decomposed completely in a vacuum, leaving nothing but lime. Dry reactions, at high temperatures, yield calcium cyanamide, but no cyanide.

Work done in the writer's laboratories confirmed the observations of other workers as summarized above.

On consideration of the probable properties which dry alkaline earth cyanides might possess, it seemed logical to suppose that if water could be largely eliminated and a reaction found that would not involve the formation of water, such cyanides might be produced. Among the commercially available compounds, calcium carbide seemed a logical source of calcium. Considering the weakly acid properties of hydrocyanic acid we should expect the reaction

$$CaC_2 + 2HCN \rightarrow Ca(CN)_2 + C_2H_2$$

Or again, if anhydrous hydrocyanic acid should not react on calcium carbide directly, then a slight amount of water should catalyze the reaction and calcium cyanide should result without introducing or forming a deleterious amount of water,

$$CaC_2 + 2H_2O \rightleftharpoons Ca(OH)_2 + C_2H_2$$
$$Ca(OH)_2 + 2HCN \rightleftharpoons Ca(CN)_2 + 2H_2O$$

the water being catalytic and the reactions continuing in cycles.

Numerous experiments soon confirmed the latter supposition. Hydrocyanic acid containing a slight amount of water reacts readily with calcium carbide, liberating acetylene and forming calcium cyanide. The reaction proceeds rapidly and smoothly to completion, and is quite similar in this respect to the action of water on carbide. The reaction between anhydrous hydrocyanic acid and fresh carbide is extremely slow.

The speed of the reaction increases with increased amounts of water. However, an excess of water is to be avoided, since it tends to increase the amount of polymerization of the hydrocyanic acid and yield a product with lower cyanogen content. An amount of water equivalent to about 2 per cent (calculated on the weight of the carbide) gives very rapid reaction and yields a product of high cyanogen content, with only slight polymerization.

It appears that the reaction is not exactly in accordance with the equations given above, but rather may be summed up as

$$CaC_2 + 4HCN \rightarrow Ca(CN)_2.2HCN + C_2H_2$$

or in reality this reaction may be entirely analogous to the formation of calcium bicarbonate—i. e., the compound formed may be $CaH_2(CN)_4$.

Raw Materials

The raw materials used are commercial calcium carbide and liquid hydrocyanic acid containing a slight amount of water as catalyst.

The hydrocyanic acid is made by a nitrogen fixation process,[3] which may be briefly outlined as follows:

> A mixture of finely divided carbon, soda ash, and about 2 per cent iron as catalyst is fed into the upper end of an inclined revolving furnace. The temperature is maintained within the furnace in the neighborhood of 1000° C. while nitrogen is passed through the mixture. Discharges of a furnace product containing 30 to 40 per cent sodium cyanide are made at intervals. The furnace product is then ground fine through a ball mill. To this finely ground material there is added the necessary finely divided carbon to make up for that lost in the reaction. There is also added just sufficient water to moisten the material and supply the necessary hydrogen to form hydrocyanic acid in the next operation. The mixture is then spread upon a tray within a specially designed gas-tight generator, and carbon dioxide passed through the mass, the reaction being as follows:
>
> $$2NaCN + CO_2 + H_2O \rightleftharpoons Na_2CO_3 + 2HCN$$
>
> The gases leaving the generator pass through a condenser cooled by brine. In this condenser the hydrocyanic acid is liquefied and withdrawn; the excess carbon dioxide passes on to a storage tank, from which it is drawn to treat a subsequent batch of material. The mass left in the generator is of the proper composition for charge material for the furnaces, except that it contains from 5 to 10 per cent of moisture. This moisture is removed by passing the mixture through a rotary drier, from which it is returned to the furnaces, thus completing the cycle.
>
> Flue gas from the furnaces is scrubbed to obtain carbon dioxide, which is used in the generator operation; the residual nitrogen is that used for fixation in the furnaces.
>
> The mechanism of the formation of cyanides when a mixture of alkali metal compounds and carbon is treated with nitrogen has been the subject of a great deal of discussion over a period of many years. It seems, however, to have been finally cleared up by some very careful and thorough experimental work carried

[1] Received January 5, 1926. Presented before the New York Section of the American Chemical Society, New York, N. Y., January 8, 1926.

[2] Patent applications pending.

[3] F. J. Metzger, U. S. Patents 1,322,195; 1,385,336; 1,388,586; 1,473,826; and 1,498,637.

out by Guernsey and Sherman[4] in the Fixed Nitrogen Research Laboratory of the U. S. Department of Agriculture.

These investigators showed conclusively that the reaction proceeds in three stages. In the first stage sodium carbonate is reduced by carbon to form metallic sodium and carbon monoxide.

$$Na_2CO_3 + 2C \rightleftharpoons 2Na + 3CO$$

In the second stage sodium in the vapor phase reacts with carbon to form sodium carbide.

$$2Na + 2C \rightleftharpoons Na_2C_2$$

In the third stage sodium carbide in the vapor phase adds nitrogen to form sodium cyanide.

$$Na_2C_2 + N_2 \rightleftharpoons 2NaCN$$

The authors show that iron acts as catalyst only in the third reaction.

Manufacture

At the plant of the California Cyanide Company, where calcium cyanide is being manufactured, a vacuum crystallizer has proved well adapted for the purpose. The writer's company is using standard vacuum crystallizers 6 feet in diameter. Each crystallizer is equipped with two gas-tight hoppers, one for feeding the carbide mechanically by means of a worm directly into the crystallizer, the other for the purpose of adding any desired substance to the compound. The vapor and gas line leads from the crystallizer through a surface condenser cooled by brine. These crystallizers take normally a charge of 300 pounds of carbide and yield about 600 pounds of finished product.

The acetylene gas leaving the condenser still contains a small amount of hydrocyanic acid gas and is passed through a scrubber in which dilute alkali is circulated to remove the last traces of hydrocyanic acid.

In making a batch the carbide hopper is charged with 300 pounds of finely ground carbide. A vacuum pump exhausts the air from the system and approximately 900 pounds of pure liquid hydrocyanic acid containing about 6 pounds of water (2 per cent on the weight of carbide) are drawn from a weighing container into the crystallizer. The agitator is started and cold water is circulated through the jacket of the crystallizer. The carbide is fed mechanically from the hopper into the crystallizer at such a rate that the entire 300 pounds are introduced in $^1/_2$ to $^3/_4$ hour. A rapid evolution of acetylene takes place and the entire reaction is completed in $^3/_4$ hour to 1 hour after the initial introduction of the carbide. At this stage the mixture in the crystallizer is nearly white and resembles ordinary acetylene sludge. Warm water is then substituted for the cold water in the jacket of the crystallizer, agitation is continued, and the excess of hydrocyanic acid evaporated. Slight discoloration of the product takes place as evaporation proceeds, and at the completion of the drying there remains a light, very finely divided powder of light tan color. The material is then discharged from the crystallizer into air-tight containers. The excess hydrocyanic acid which has been evaporated off and condensed is returned for the treatment of a subsequent batch.

When it is desired to add other materials, such as sulfur, arsenate of lead, etc., these substances are added through the second hopper during evaporation of the excess liquid hydrocyanic acid. The total time required to produce a batch as described is from 3 to 4 hours.

Properties

As may be seen from the method of manufacture, the finished product contains only such impurities as are common to calcium carbide, together with the small amount of polymer which is responsible for the color of the compound. It is in an extremely fine state of subdivision and therefore is admirably adapted for dusting purposes. The cyanogen content will vary somewhat, depending upon the quality of carbide employed in its manufacture and the details of manipulation; it will, however, range between 52 and 58 per cent, averaging about 55 per cent, the latter being equivalent to 103.6 per cent sodium cyanide.

The product is readily soluble in water, evolving a small amount of heat. The water solution gives the characteristic reactions for calcium and cyanogen ions. The product is also readily soluble in ordinary ethyl alcohol and in methanol both in their absolute and dilute forms.

The product is stable when heated to temperatures up to 100° C. It begins to decompose slightly at about 120° C. It remains unchanged when exposed (in air-tight containers) over long periods of time at temperatures ranging from freezing to 60° C. (140° F.).

The product is extremely sensitive to moisture, being decomposed with the liberation of hydrocyanic acid.

$$CaH_2(CN)_4 + 2H_2O \rightarrow Ca(OH)_2 + 4HCN$$

The moisture of the air liberates hydrocyanic acid very rapidly, so much so that when spread in extremely thin layers about three-quarters of the hydrocyanic acid content has been evolved in half a minute and practically all of it in one minute. Such evolution of gas takes place on exposure to air even when the humidity is 25 per cent or less. The reaction with atmospheric moisture is so rapid that the evolved gas may be readily ignited.

Uses

From the properties just described it is obvious that calcium cyanide is particularly suitable for such operations as have hitherto been accomplished by means of liquid or gaseous hydrocyanic acid. Its extremely fine state of subdivision makes distribution of the gas a simple operation. The product has many advantages over liquid hydrocyanic acid, notably in its safety in handling, transportation, and application. The powder is perfectly stable under all ordinary conditions of storage and transportation, provided only that it be protected from atmospheric contact. On the contrary, liquid hydrocyanic acid is dangerous to handle, and it is difficult and dangerous to transport since it is subject to spontaneous polymerization which may result in violent explosions. Since mere exposure to the air liberates hydrocyanic acid freely and practically quantitatively from calcium cyanide in a very short time, this new product has been called "powdered hydrocyanic acid."

The citrus industry struggles constantly against a pest known generally as scale. Hydrocyanic acid gas obtained in various ways has been used for combating this pest for many years. The common practice at present is the application of liquid hydrocyanic acid under tents placed over the trees. The industry is, however, confronted with the fact that there is a comparatively narrow margin between the dosage which controls the scale and that which injures the fruit or tree or both. It has long been known, also, that the ranges of toxicity of liquid hydrocyanic acid for plant and animal life approach coincidence much more quickly in daylight than in darkness; the same applies to damp or foggy atmospheric conditions. Hence, in practice, such fumigation is carried out at night in comparatively dry weather. When calcium cyanide is used for fumigation—as, for instance, by dusting it under the fumigating tents—field experiments have demonstrated that a satisfactory kill of the scale, without injury to fruit or tree, can be secured by the application of much less total cyanogen than would be contained in the liquid hydrocyanic acid dosages which have been established as standard by scientific experiment as well as by years of prac-

[4] *J. Am. Chem. Soc.*, **47**, 1932 (1925).

tical experience. Field work has demonstrated also that no "burning" of foliage takes place with calcium cyanide, even when concentrations are used much in excess of the corresponding standard dosage of liquid hydrocyanic acid. It has been repeatedly noted that leaves may be thickly coated with the powder itself without any burning being observed.

Since the margin of safety is so much wider when using calcium cyanide, it follows that the number of hours out of the twenty-four which may be used for fumigation may be greatly extended by the use of "powdered hydrocyanic acid." This assumption has been amply borne out by numerous field experiments with daylight fumigation as well as in wet and foggy atmospheres.

The wider range of toxicity of the new product over liquid hydrocyanic acid has the further advantage that it makes possible the eradication of the so-called "resistant scales" which occur in many sections of California. These resistant scales so far have not only survived the highest standard dosage of liquid hydrocyanic acid, but even excess treatment up to defoliation of the tree has failed to secure satisfactory control.

It has been repeatedly demonstrated in field work with "powdered hydrocyanic acid" that there is a difference in the manner in which the scale are killed by the new product. Scale killed by liquid hydrocyanic acid present at first no change apparent to the eye, but after several weeks gradually dry up. On the other hand, when the new product has been used, a decided change in appearance is evident within 6 days and the dead insects have been found to be swelled up or bloated, a condition which has not been observed when killing with liquid hydrocyanic acid.

"Powdered hydrocyanic acid" lends itself to all sorts of fumigation, such as warehouses, ships, mills, railroad cars, etc. Where it is not objectionable to blow the dust into the space to be fumigated, suitable dust guns may be used. On the other hand, the dust may be spread along the floor, through the aisles, or similarly in very thin layers and in predetermined amounts by suitable appliances, or air may be blown through the dust, held in a suitable filtering receptacle, such as a bag.

No doubt many new applications of the new product will be found. On account of its ready solubility in water and a number of organic solvents, numerous applications of "powdered hydrocyanic acid" suggest themselves.

Acknowledgment

The author wishes to acknowledge the assistance of R. W. Poindexter, Jr., of the California Cyanide Company, and of his associates, C. E. Swift and P. T. Dolley, in carrying the operations from the laboratory to full-scale plant production.

Dewar Flasks in Physical Chemistry Laboratory Exercises[1]

By Aubrey C. Grubb

University of Saskatchewan, Saskatoon, Canada

IN MOST laboratory manuals the procedure for the determination of the heat of neutralization of acids and bases in dilute solution involves considerable chance of error for the average student in physical chemistry. In the first place the calorimeter of the Fritz Kohler type or a "modification of that devised by Thomson" demands most careful manipulation to eliminate errors due to radiation, heat capacity of the apparatus, and lag effects. Secondly, the students are instructed to use two thermometers, previously compared, one in acid and the other in the alkali. Then at a certain instant one solution is poured into the other. Serious errors are usually found in this part of the work and consistent results are difficult to obtain, owing chiefly to the large personal equation.

In 1921 an attempt was made in this laboratory to use the method described by Mathews and Germann[2] using a Dewar flask for the calorimeter and introducing down the center a glass tube, containing one of the reagents, closed at the bottom by a piece of rubber. The acid and base were left in the Dewar and stirred slowly until a regular slow change in the temperature reading of the Beckman showed the solutions to be near temperature equilibrium. At this point the rubber was punctured and the total heat change determined.

It was found exceedingly difficult to fasten the rubber securely enough over the end of the glass tube so that diffusion did not take place or no acid or alkali came in contact. To avoid this difficulty a thin bulb was blown at the end of the tube. The bulb can be made thin enough to allow temperature equilibrium to take place much quicker than by using the rubber diaphram. The bulb also eliminates any errors due to diffusion of the two solutions. At the proper instant a slight stroke from the projecting end of the glass stirrer will rupture the bulb and allow the acid and base to mix freely. The maximum temperature change is then quickly ascertained. The advantages of the all-glass apparatus, in spite of the variation in specific heat, are pointed out carefully by White.[3]

The student can use carefully prepared and standardized acid and alkali to determine the heat capacity of the calorimeter. These values are found to be consistent and very low when compared with the all-metal calorimeter. Moreover, only one thermometer is necessary, which eliminates the chance for error where two instruments are used. The low heat conductivity of the glass vessel adds to the accuracy of the reading for the total temperature change of the mixed solutions. Furthermore, this set-up can be made in much shorter time, stirring can be less vigorous, and, lastly, the students gain some knowledge of the rudiments of cutting and working glass. The jackets of old condensers have been found very suitable for use as central tubes, as they are about the correct diameter for the liter Dewar and have quite thin walls.

This method has been used with very satisfactory results since 1921 at the University of Saskatchewan for the determination of various heats of reaction.

[1] Received November 16, 1925.

[2] *J. Phys. Chem.*, **15**, 73 (1911).

[3] *J. Am. Chem. Soc.*, **40**, 1890 (1918).

Adsorption Studies on the Decolorization of Mineral Oils[1]

By T. H. Rogers, F. V. Grimm, and N. E. Lemmon

STANDARD OIL COMPANY (INDIANA), WHITING, IND.

Although the decolorization of mineral oils by porous materials is generally considered to be due to adsorption, it has not previously been shown whether the laws of adsorption are applicable. Decolorization experiments, using a number of kinds of oils and several adsorbents, show that Freundlich's equation applies accurately, when amount of color removed is used as a measure of amount of material adsorbed.

Color measurements are expressed on a true color scale and details of the technic of color measurement are described. The slopes of the color adsorption curves vary widely for different oils; those for kerosene differ essentially from the well-established characteristics of typical adsorption. The significance of such abnormalities is discussed. It is shown that color formation of cracked kerosene in the presence of clay is due to oxidation.

THE use of various porous materials, particularly fuller's earth, for the decolorization of mineral oil products has been a common refinery practice for many years. Although the action of such materials has been ascribed to chemical reaction by Löb,[2] various authors[3] have concluded that the action is wholly mechanical. Day[4] has pointed out that, in addition to decolorization, fuller's earth effects marked changes in the composition of crude oils, which he regards as due to the selective action of capillary diffusion. Parsons[5] has suggested that the decolorization of oils by fuller's earth is due to adsorption, and subsequent work, especially that of Gurwitsch,[6] has led to a general acceptance of this point of view. However, except for the recent article of Dunstan, Thole, and Remfry,[7] but little quantitative data have been published and no effort has been made to analyze data on the decolorization of mineral oils from the standpoint of the general laws of adsorption.

It is the purpose of this article to describe a convenient and quantitative method of studying the decolorization of mineral oils, to analyze such data in comparison with typical cases of adsorption, and to discuss color formation in the presence of clay, especially in cracked distillates.

Methods

COLOR MEASUREMENT—It is necessary to have an accurate means of measuring color and a rational scale for expressing the determinations. Such requirements are largely satisfied by the method developed by Parsons and Wilson,[8] in which the color of the oil is compared with that of a standard oil in a Duboscq colorimeter. The color of the standard oil is determined by comparison with a Lovibond color glass, and color values are expressed in terms of this primary standard, being inversely proportional to the depth of the oil. According to Beer's law, these color units are therefore proportional to the concentration of the coloring matter and may be taken as a measure thereof.

Considerable care must be exercised in the choice of the standard oil, for it has been found that use of a single oil for the whole range of color, involving the measurement of different kinds of oil, will give only approximate color values. Unless the oil being measured and the standard match exactly when brought to equivalent depths, the ratio of depths found will vary according to the depth taken. That is, with two solutions of cylinder stock, apparently quite the same in hue, but differing appreciably in "grayness," it was found that the oils matched at depths of 6.32 and 1.1 mm., respectively, while using a deeper range the depths when the oils matched were 12.75 and 2.0 mm., respectively. The ratio between the two oils is thus not constant, being 5.75 in the first case and 6.37 in the second. It was demonstrated that this difference was not caused by inaccuracy due to the greater "grayness" of one of the oils, as substantially the same result was obtained with or without a compensating shading (use of a frosted glass under the lighter oil). Such discrepancies are still more marked if different kinds of oil, which have roughly but not exactly the same color, are used for the standard and unknown oil—as for instance, the use of a cylinder stock solution as standard in measuring the color of a red oil.

To obviate these difficulties different standard oils were used, choosing as a standard for each series of oils an oil identical with those under investigation, of such a color that it could be matched at a convenient depth with the Lovibond 42 glass. Approximately this same depth of standard was thereafter used in comparing it with the unknown oil. Since it was demonstrated that Beer's law applies accurately when two oils that match perfectly are being compared, this procedure eliminates the inaccuracies referred to above.

For the purpose of orientation reference may be made to Figure 1,[9] which shows the relation of the true color values to the various color systems in common use. This was obtained by making up solutions of filtered cylinder stock in naphtha to match each point of the A. S. T. M. color system. The color of these oils was then measured on the Tag-Robinson colorimeter and also by the true color method, to obtain the relation between the three systems. The relation of the Saybolt system was obtained by measuring the true color of a Saybolt color disk. Only a portion of the Saybolt range is shown on the chart; the remainder may be readily calculated by using the value 0.0256 for the true color of a 25 color oil. Owing to differences in the light absorption of the color glasses used in the four different color systems, an oil made up to

[1] Presented before the Division of Petroleum Chemistry at the 69th Meeting of the American Chemical Society, Baltimore, Md., April 6 to 10, 1925. Received September 30, 1925.

[2] *Chem. Rev. Fett-Harz-Ind.*, **15**, 80 (1908).

[3] Engler and Albrecht, *Z. angew. Chem.*, **36**, 889 (1901); Grafe, *Petroleum Z.*, **3**, 292 (1907).

[4] *Proc. Am. Phil. Soc.*, **36**, 112 (1897); THIS JOURNAL, **1**, 449 (1909).

[5] *J. Am. Chem. Soc.*, **29**, 598 (1907).

[6] "Wissenschaftliche Grundlagen der Erdölverarbeitung," 2nd ed., **1924**, p. 337. Julius Springer, Berlin.

[7] *J. Soc. Chem. Ind.*, **43**, 179T (1924).

[8] THIS JOURNAL, **14**, 269 (1922).

[9] This chart was described in a paper presented by T. H. Rogers before the Petroleum Division of the 68th Meeting of the American Chemical Society, Ithaca, N. Y., September 8 to 13, 1924.

match exactly a color glass of one of the systems will be "off" shade when compared even at the proper depth with a color glass of each of the other three systems. Therefore, in view of what has been said above, it is apparent that a somewhat different relation between the systems will be obtained depending on the oil used for an intercomparison. The relations shown in Figure 1 are fairly exact and are reproducible when dealing with cylinder stock solutions such as was used in making the comparison; however, for general use the relations are only approximate and cannot be taken as absolute.

Decolorization Experiments—The so-called contact method of decolorization was used in all the experiments reported in this article. The oil was agitated with the adsorbent in a mechanical shaker, then filtered through a Büchner funnel and the color of the filtrate determined. The experiments were carried out at room temperature with the exception of those with wax and red oil, which required a temperature of 66° C. (150° F.). The time of contact required to reach equilibrium between the adsorbent and oil varied between 10 and 60 minutes and was determined for each series of experiments. The adsorbents, which were finely divided materials of about 200 mesh, were dried by heating to suitable temperatures.

Application of Freundlich's Adsorption Equation

In the development of a suitable method for comparing various adsorbents for decolorization of mineral oils, it was found that the application of Freundlich's equation[10] offered many advantages over the more common methods in general use. The equation is

$$\frac{x}{m} = KC^{1/n}$$

where x = the amount adsorbed by m grams of the adsorbent, C = equilibrium concentration, and n and K are characteristic constants. Applying this to decolorization results, x = units of color removed, m = grams of adsorbent per 100 grams of oil, and c = equilibrium color. This gives arbitrary values depending on the units chosen, but the value of n will not vary provided a color scale in which the values are additive is used. Expressing this equation as

$$\log \frac{x}{m} = \log K + \frac{1}{n} \log C$$

and plotting the values of $\log x/m$ against $\log C$, a straight line having a slope of $1/n$ is obtained.

The straight-line curves plotted in Figure 2 show that Freundlich's adsorption equation is an accurate expression of the experimental results tabulated in Table I. Particular care was exercised in the color determinations in order to test accurately the applicability of Freundlich's equation. A slight error in the color determination of the original oil causes a curvature in the upper portion of the curve but does not affect appreciably the lower portion.

Table I—Decolorization of Cylinder Stock Solution with Clay

Grams adsorbent per 100 grams solution	Equilibrium color	$\frac{x}{m}$ values
Adsorbent A with 260 Color Solution		
5.0	204	11.2
10.0	154	10.6
20.0	84	8.8
25.0	60	8.0
33.3	37	6.7
50.0	13.6	4.93
Adsorbent D with 263 Color Solution		
5.0	219	8.7
10.0	189	7.4
20.0	131	6.6
22.8	120	6.26
33.3	86.5	5.3
46.8	56.5	4.4
50.0	53.3	4.19
80.0	26.2	2.96

Comparison of Various Adsorbents for Decolorization

Three widely different petroleum products were used for the comparison of the different adsorbents—namely, a straight-run kerosene, paraffin wax, and a naphtha solution of cylinder stock. The adsorbents A, B, C, and D are clays obtained from different sources, E and F are activated carbons, and G is an inorganic gel. The results are shown in Figures 3, 4, and 5. The convenience of this method of plotting results may be emphasized, since with a minimum of tests the amount of adsorbent required for a given degree of decolorization may be calculated.

[10] "Kapillarchemie," 3rd ed., **1923**, p. 232. Leipzig.

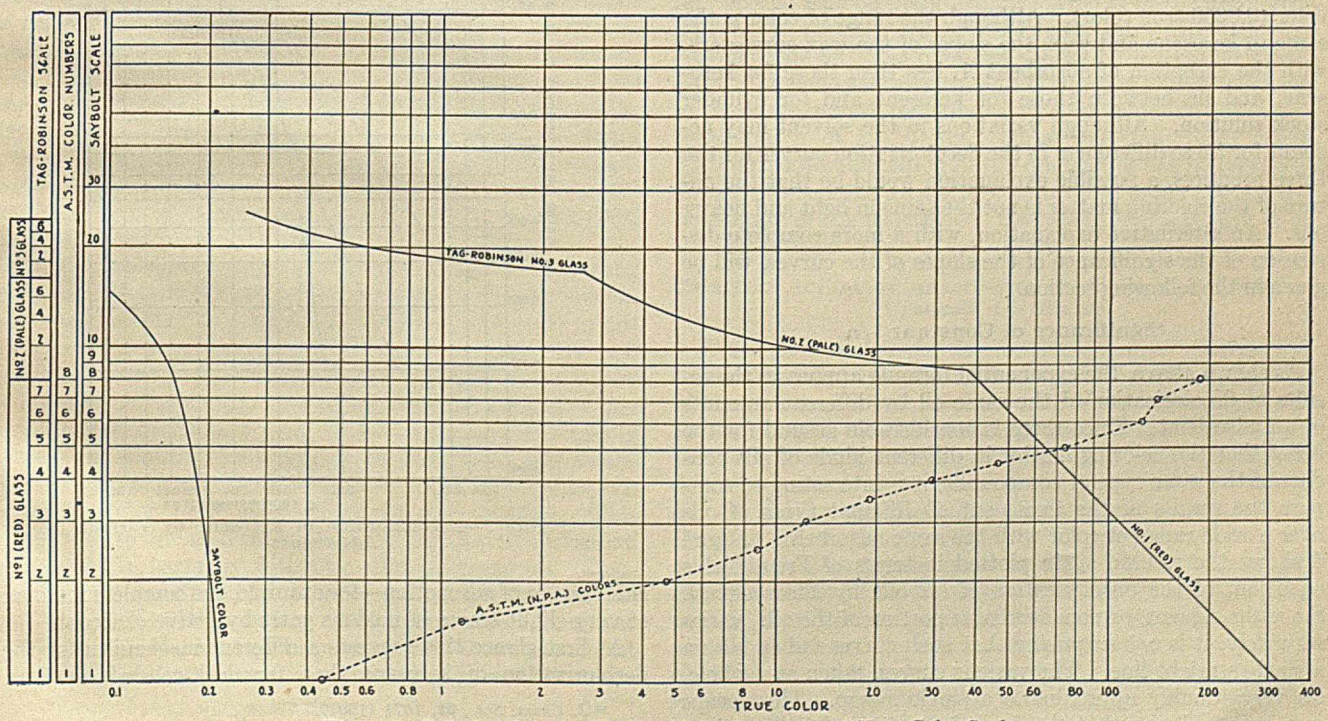


Figure 1—Relation between Various Color Systems and True Color Scale

It is to be observed that the order of decolorizing power for the clays is the same in the three cases. On the other hand, the activated carbons are effective adsorbents for the darker colored compounds contained in the heavier oil, and have but slight affinity for the coloring matter present in kerosene. Furthermore, the choice of the most suitable adsorbent for a given oil depends in some cases upon the amount of coloring matter to be removed. For example, adsorbent *G* is a good adsorbent for refining kerosene to a 21 Saybolt color (0.0426

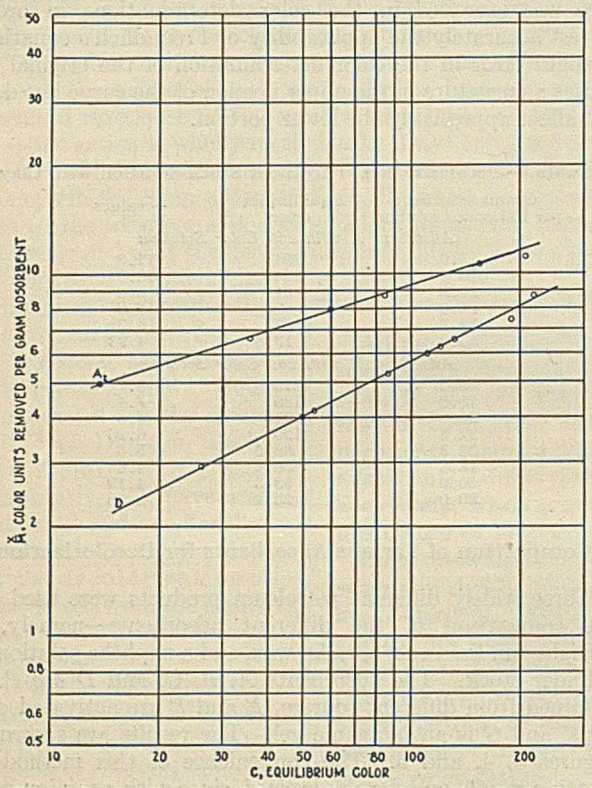


Figure 2—Application of Freundlich's Adsorption Equation to Decolorization of Mineral Oil

true color), but is very poor for refining the oil to 25 Saybolt color (0.0256 true color). Although the range of color is the same in kerosene and wax, the slopes of the wax curves are, with the exception of adsorbent *A*, less than those for kerosene, and lie between those for kerosene and for cylinder stock solution. Although variations in the solvent may account for these differences in the decolorization curves for the three products, a possible explanation would be that the nature of the coloring matter is not the same in light and heavy oils. An alternative explanation, with a more complete discussion of the significance of the slopes of the curves, will be given in the following section.

Significance of Constant $1/n$

As shown above, the exponential formula applies to the results of decolorization of the same oil by different amounts of an adsorbent. Since there is considerable ground for the belief that the coloring matter in different kinds of oils consists of the same type of compounds, it is interesting to compare the results of the treatment of different types of oils over a wide range of color with the same adsorbent. Figure 6 shows the results, again plotted in terms of Freundlich's equation, of the decolorization of six oils by adsorbent *D*. Since the solvent, or nonadsorbable portion of the oils, varies so widely, it is not surprising that such curves fail to fall on a single straight line. The various curves, taken as a whole, do very roughly approximate a single sweep. This means in a practical way that the ease of decolorization of various products is, on the basis of adsorption theory, of the same order of magnitude. However, the most striking feature is the marked variation in the slopes of the curves (values of $1/n$). The slopes increase in a regular way as one passes from darker to lighter oils. The significance of this is much more clearly seen when these curves are plotted on ordinary coördinate paper (Figure 7). In this case for comparative purposes amounts adsorbed and equilibrium concentrations are expressed in per cent of original concentrations. Only the curves of greatest and least slope are included, and for comparison there are plotted the results of Davis[11] on the adsorption of iodine from toluene solution by charcoal. All known cases of true adsorption have curves similar to the latter. Freundlich[12] cites over twenty cases of adsorption from solution, in all of which the values of $1/n$ are between 0.24 and 0.55, whereas the values of $1/n$ for the oils in Figure 6 vary from 0.53 to 2.2. The slopes of the curves for cylinder stock, red oil, technical white oil, and pale oil are larger than those from most adsorption data, but are still less than one; this according to Freundlich's definition indicates adsorption. However, the decolorization of kerosene is absolutely out of that category. It is typical of adsorption that the amount adsorbed is relatively greater in lower concentrations—i. e., is proportional to a root of *C*—while in this case the amount adsorbed is relatively greater the more concentrated the solution—is proportional to a power of *C*. The practical result of this is the extreme difficulty of completely decolorizing kerosene. As a matter of fact, this is never attempted in refinery practice, whereas it is interesting to note that in other practical applications of adsorptive materials the basis for their use is the utilization of this character-

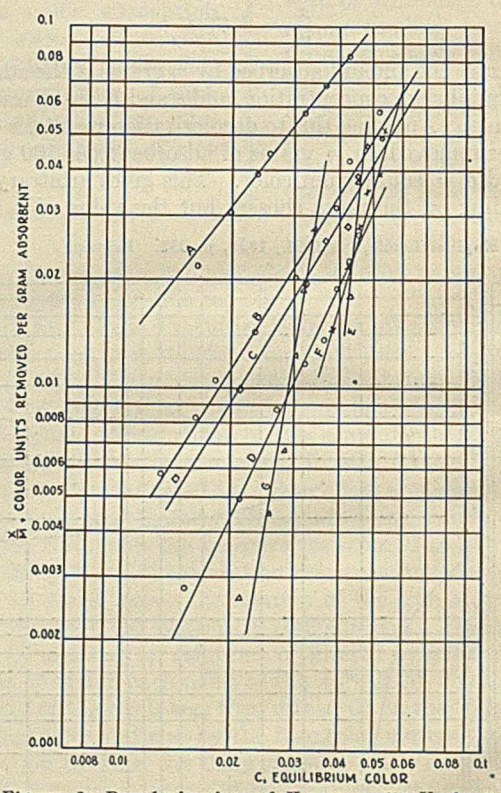


Figure 3—Decolorization of Kerosene by Various Adsorbents

istic feature of adsorption—for example, the complete removal of very slight traces of noxious gases by active charcoal.

At first glance this suggests a different mechanism for the decolorization of kerosene than for dark-colored oils. In

[11] *J. Chem. Soc.*, **91**, 1671 (1907).
[12] *Loc. cit.*, p. 236.

making this comparison, however, it is wise to bear in mind the assumptions that have been made in applying the exponential formula to decolorization results. When dealing with reversible adsorption of a single known substance, as is the case for the examples of typical adsorption cited, determinations are made and results are expressed in terms of actual amounts of material adsorbed, whereas in decolorization

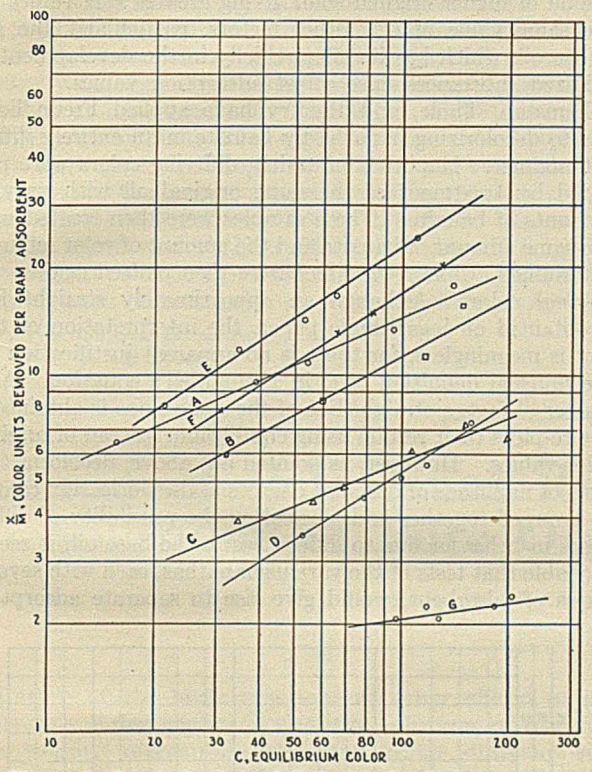


Figure 4—Decolorization of Cylinder Stock Solutions by Various Adsorbents

experiments the color is used as a measure of the concentration of colored substances—probably a complex mixture of chemical individuals in colloidal[13] solution. No account is taken of other noncolored bodies adsorbed, or of the presence of colored substances formed in contact with the adsorbent, which Gurwitsch[14] has shown to be an important feature. The ratio of the color removed by adsorption to the total amount of material adsorbed will therefore be quite variable, depending on the quality of the oil being investigated. Since a measure of only an indefinite part of the total amount adsorbed is being obtained, it is indeed surprising that the exponential formula applies so well even under certain fixed conditions.

Altogether, these considerations indicate that the abnormal values of the slopes of these decolorization curves do not necessitate the conclusion that decolorization is not due to adsorption, and a continuation of the same point of view will provide a possible explanation of the variation in the values of $1/n$ with different oils. Assuming that the amount of material formed by contact with the adsorbent and irreversibly adsorbed is constant for each gram of adsorbent, this means that a constant value should be added to the x/m values obtained by difference in color before and after treating. This would tend to diminish the slope of the logarithmic curves and bring them in harmony with true adsorption curves. Passing from the treatment of dark-colored to light-colored oils it is reasonable to expect that the amount adsorbed, as the writers measure it, is a smaller proportion of the total amount adsorbed. Thus, the constant value to be added will be relatively much larger than in the case of dark-colored oils, which accounts for the very steep slope of the kerosene curves. In line with this explanation is the fact that the curves for the decolorization of wax and technical white oil, products which are more highly refined and would be expected to contain less reactive material, are much flatter than those for oils in the same color range.

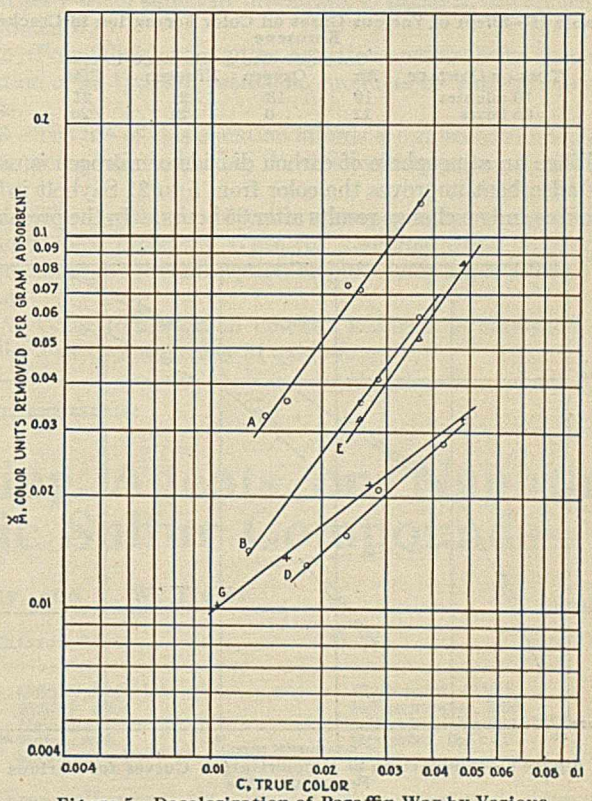


Figure 5—Decolorization of Paraffin Wax by Various Adsorbents

Another interesting fact brought out in Figure 6 is that the colored bodies are not homogeneously adsorbed. The curve for "special pale oil" represents the results of the decolorization of a partially decolorized pale oil. Although this "special pale oil" was obtained simply by a treatment with clay of the same pale oil whose decolorization values are shown in the curve immediately above, its x/m values do not form a continuation of the original curve, but fall much below. The partial decolorization of the original oil has rendered the oil more difficult of further decolorization, indicating a selective action of the adsorbent. Such behavior is typical of all the oils studied.

Catalytic Action of Adsorbents on Color Formation in Cracked Distillates

While determining the decolorizing action of adsorbent *D* on a cracked kerosene, it was observed that with a short time of contact the oil was decolorized to about the same extent as the straight-run kerosene reported above. However, if the oil was left in contact with the clay, color was rapidly developed and finally exceeded the color of the original oil. A similar catalytic effect of bauxite was reported by Dunstan, Thole, and Remfry.[7]

Although color formation in cracked distillates is usually considered to be due to polymerization of unsaturated compounds, no definite experimental evidence has been reported on this question. In order to determine whether oxygen is essential to color formation, several comparative experiments were carried out with and without the presence of oxygen. This was accomplished by carefully replacing the

[13] Rakusin, *Petroleum Z.*, **4**, 922 (1908).

[14] *Loc. cit.*, 372.

air in the clay and oil with an inert gas and maintaining an atmosphere of this gas during the time of contact. In these experiments, 10 grams of clay and 150 grams of cracked kerosene (5 Saybolt color) were used. Four gases were investigated for their effect on color formation—air, oxygen, nitrogen, and carbon dioxide. In each case the oil was shaken for two different periods of time, 10 minutes and 65 hours.

Table II—Effect of Various Gases on Color Formation in Cracked Kerosene

Time of Contact	Color of Oil in Saybolt Units			
	Air	Oxygen	Nitrogen	CO_2
10 minutes	19	18	21	21
65 hours	12	0	21	20

When an atmosphere of carbon dioxide or nitrogen is used the adsorbent improves the color from 5 to 21 Saybolt in 10 minutes and no change results after 65 hours. In the presence

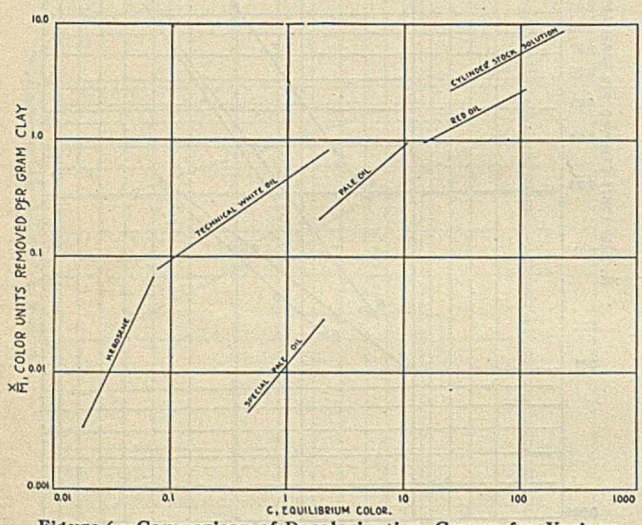


Figure 6—Comparison of Decolorization Curves for Various Petroleum Oils

of air and oxygen some color is formed in the first 10 minutes and at the end of 65 hours the color formation is very noticeable. Although it is certain that under these conditions color formation is due to oxidation, it does not follow that polymerization does not also occur. Under widely different conditions, such as the vapor phase treatment with clay, it is quite probable that the reaction is entirely due to polymerization.

Numerous experiments have shown that the catalytic action of clay is much more pronounced on an oil which has previously been partially decolorized. For example, the oil used in the above experiment had developed a color of from 21 to 5 Saybolt units on aging in the presence of air for about 3 months. If this oil is first decolorized to 21 color and then treated with a fresh portion of clay, the color is increased to 6 Saybolt units in 3 hours, as compared with 12 color in 65 hours for the original oil. It is also to be noted that the adsorbents differ greatly in their catalytic action on color formation and that the action is not proportional to their decolorizing power. Adsorbent *D* possesses the greatest catalytic activity, whereas adsorbents *C* and *G* are practically noncatalytic.

Discussion

Since it has been emphasized that Freundlich's formula fits the results of decolorization experiments, it may be well to point out the limitations of its use. In general, only the results of decolorization of a single oil by different amounts of adsorbent can be grouped together. The conditions are not those of simple solution of a solute in a single solvent, so that results of tests on an oil diluted with colorless naphtha are not comparable with those on the original oil, even if the amount of adsorbent is expressed correctly in relation to the amount of original oil. Also, it has already been shown that decolorization of a partially decolorized oil gives results widely different from the original oil. In fact, two oils of the same kind, produced by the same refinery operations but differing considerably in color, will give different adsorption curves, the oil of higher original color giving greater x/m values for the same value of C. Other factors, particularly the age of the oil, which has its effect chiefly in the development of oxidized substances, also affect adsorption values.

Dunstan, Thole, and Remfry have applied Freundlich's law to decolorizing naphtha by bauxite in an entirely different manner. Naphthas of widely differing colors were prepared by treatment of the same original oil with varying amounts of bauxite. These samples were then treated with the same amount of bauxite and the amount of color removal determined. The x/m values were then plotted against the *original* colors. Although an approximately straight line is obtained on logarithmic paper, the interpretation of this fact is meaningless, for there is no apparent justification for the unusual definition of C in Freundlich's equation. As a matter of fact, a straight line of the same slope is obtained if one re-plots their results using equilibrium instead of original color values. However, as pointed out above, decolorization tests of naphthas of different degrees of decolorization cannot be grouped together and, neglecting the possibility of differences in behavior due to differences in the base oil, it seems probable that tests of the various naphthas, each with several ratios of adsorbent, would give rise to separate adsorption

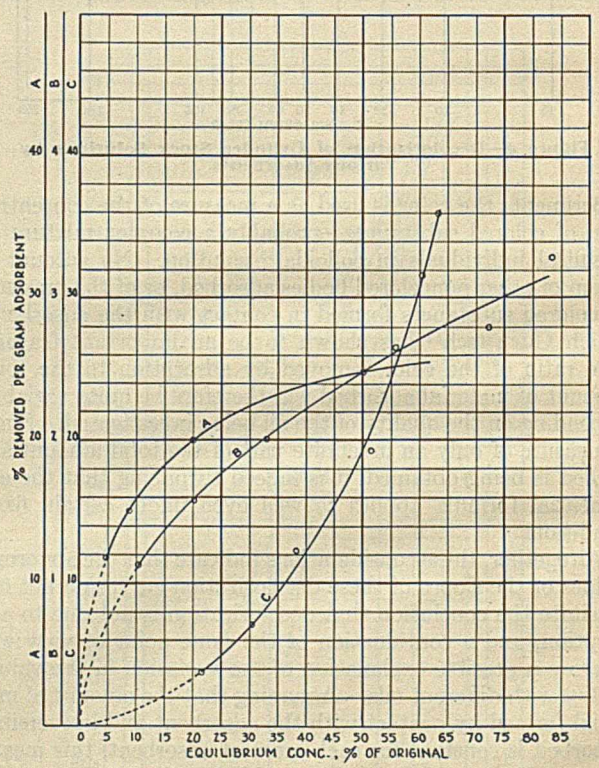


Figure 7—*A*—Adsorption of Iodine from Toluene Solution by Charcoal; *B*—Adsorption of Coloring Matter from Cylinder Stock Solution by Clay; *C*—Adsorption of Coloring Matter from Kerosene by Clay

curves for each naphtha, falling below each other in the order of their original colors. Guiselin[15] apparently accepts Dunstan's interpretation of the Freundlich equation, although he points out that it leads to the erroneous conclusion that the result of a single treatment of an oil with a given amount of

[15] *J. Inst. Petroleum Tech.*, **10**, 923 (1924).

adsorbent is superior to that of treatment of the oil with the same total amount of adsorbent in successive portions.

In a preceding section the writers' decolorization results were compared with the adsorption of pure substances from a simple solvent. There are, however, examples which approach much more closely the conditions for decolorization of mineral oils. These are especially the decolorization of sugar solutions and of vegetable oils. Sanders[16] and Teeple and Mahler[17] have recently shown that the decolorization of these substances follows Freundlich's law, and a striking similarity between their curves and those in Figures 3, 4, and 5 is at once apparent. The slopes of the adsorption curves given by Sanders for sugar solutions are around 0.6, while those given by Teeple and Mahler for vegetable oils are much like the present writers' curves for kerosene as $1/n$ varies between 0.9 and 4.1. Teeple and Mahler do not discuss the significance of these abnormal slopes. It is hardly necessary to point out that the analogy between the results of adsorption experiments on sugar solutions, vegetable oils, and mineral oils is complete; each involves the determination of the amount of unknown materials adsorbed by measurement of color removal.

[16] This Journal, 15, 784 (1923).
[17] *Ibid.*, 16, 498 (1924).

Conclusions

1—The method of color measurement of oils proposed by Parsons and Wilson is satisfactory for quantitative decolorization tests when sufficient precaution is taken in the choice of a standard.

2—Freundlich's adsorption equation applies to the decolorization of all types of petroleum products by various adsorbents.

3—The use of this equation affords a convenient and accurate method of evaluating the decolorizing power of adsorbents.

4—The slopes of the color adsorption curves for light-colored oils, especially those for kerosene, differ markedly from those for the adsorption of pure compounds from solution.

5—Color formation in cracked kerosene is catalyzed by fuller's earth and is due to oxidation.

Action of Petroleum Refining Agents on Naphtha Solutions of Pure Organic Sulfur Compounds[1]

By A. E. Wood, Clyde Sheely, and A. W. Trusty

Mississippi College, Clinton, Miss.

A study of the basic reactions or other effects of petroleum-refining agents on naphtha solutions of free sulfur, isoamyl mercaptan, hydrogen sulfide, dimethyl sulfate, methyl *p*-toluene sulfonate, carbon disulfide, *n*-butyl sulfide, *n*-propyl disulfide, thiophene, diphenyl sulfoxide, and *n*-butyl sulfone. The refining agents employed include the alkaline sodium plumbite solution (Doctor treatment), sodium hydroxide solution, silica gel, fuller's earth, aluminium oxide, and sulfuric acid of three strengths—fuming, 66 Bé., and 53 Bé.

THIS paper is a continuation of some previously reported work by Wood, Lowy, and Faragher,[2] and represents a quantitative study of the action of petroleum-refining agents on naphtha solutions of free sulfur, mercaptans, hydrogen sulfide, alkyl sulfates, sulfonic acids, carbon disulfide, alkyl sulfides, alkyl disulfides, sulfoxides, sulfones, and thiophene. The sulfoxides and sulfones have never been identified in petroleum distillates or residues. Free sulfur and the other compounds listed have been identified by various investigators in certain petroleum distillates and residues, but the evidence is not so convincing in many cases as one could wish.

The refining agents employed include sulfuric acid of three strengths—fuming, 66 Bé., 53 Bé.—sodium plumbite, sodium hydroxide, silica gel, fuller's earth, and aluminium oxide. It is hoped that investigations of basic reactions or effects of standard refining agents on naphtha solutions of typical sulfur compounds will yield information of value to the industry and thus serve to remove some of the empiricism long prevalent in petroleum-refining operations.

Materials

The naphtha used for making the solutions had the following properties:

[1] Received August 1, 1925.
[2] This Journal, 16, 1116 (1924).

Color, water-white	Flash point, 42° C.
Acidity, none	Iodine number, 3.50
Halogens, none	Initial boiling point, 152° C.
Sulfur, none	Dry point, 237° C.
Specific gravity, 0.77 at 20° C.	

Free sulfur and the organic sulfur compounds were the purest obtainable. Using the naphtha as the solvent, the following stock solutions were prepared:

Stock Solution	Per cent Sulfur
Free sulfur	0.26
Isoamyl mercaptan	0.29
Hydrogen sulfide	0.034
Dimethyl sulfate	0.04
Methyl *p*-toluene sulfonate	0.15
Carbon disulfide	0.08
n-Butyl sulfide	0.30
n-Propyl disulfide	0.38
Thiophene	0.09
Diphenyl sulfoxide	0.05
n-Butyl sulfone	0.08

General Methods

Determination of Sulfur—This was made by the lamp method as described in *Technical Paper* 298, U. S. Bureau of Mines.

Determination of Desulfurizing Effect—This was carried out in a closed system in a specially constructed apparatus which was described in detail by Wood, Lowy, and Faragher.[2] The desulfurizing effect of the refining agent was determined from the sulfur content of the naphtha solution before and after treatment. Duplicate and in many cases a larger number of experiments were made.

Effect of Sulfuric Acid

All these experiments were carried out in the previously described closed system using three strengths of sulfuric acid—fuming, 66 Bé., and 53 Bé. Fifty cubic centimeters of each naphtha stock solution were treated with 4 and 16 cc. quantities of acid of the indicated strength for 1 hour. The naphtha recovered from the acid treatment was washed

to the neutral point with a 1 per cent solution of sodium hydroxide, using phenolphthalein as an indicator.

Table I—Average Per cent of Sulfur in Naphtha Treated with Sulfuric Acid

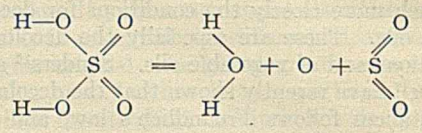
Naphtha Solution	Fuming 4 cc.	Fuming 16 cc.	66 Bé. 4 cc.	66 Bé. 16 cc.	53 Bé. 4 cc.	53 Bé. 16 cc.
Free sulfur	0.26	0.258	0.26	0.26	0.26	0.26
Isoamyl mercaptan	0.00	0.00	0.22	0.02	0.28	0.27
Hydrogen sulfide	0.03	0.03	0.03	0.03		
Dimethyl sulfate	0.00	0.00	0.00	0.00	0.01	0.008
Methyl *p*-toluene sulfonate	0.00	0.00	0.035	0.00	0.15	0.15
Carbon disulfide	0.08	0.08	0.08	0.08	0.08	0.08
n-Butyl sulfide	0.00	0.00	0.02	0.01	0.29	0.28
n-Propyl disulfide	0.00	0.00	0.16	0.02	0.35	0.34
Thiophene	0.00	0.00	0.01	0.00	0.08	0.08
Diphenyl sulfoxide	0.00	0.00	0.005	0.005	0.01	0.006
n-Butyl sulfone	0.00	0.00	0.00	0.00	0.01	0.008

An examination of Table I shows that free sulfur and carbon disulfide are not affected by sulfuric acid of any strength.

The mercaptans were readily removed by the fuming, less readily by the 66 Bé., and very sparingly, if at all, by the 53 Bé. acid. Several other strengths of acid were tried on the mercaptan solution: 16 cc. of 63 Bé. acid removed about 20 per cent of the mercaptan; 44 Bé. and 24 Bé. acid did not affect the mercaptan. These results can be readily explained on the basis of the oxidizing and solvent action of sulfuric acid. Fuming sulfuric acid, being the best oxidizing and dissolving agent, readily converts the mercaptan to the corresponding disulfide and dissolves it as such. The 66 Bé. acid is not so strong an oxidizing agent, but when used in sufficient quantity will convert and remove the mercaptan in the form of the disulfide. In the oxidation of the mercaptan to the disulfide, the alkyl acid thiosulfate and the alkyl dithiosulfate are perhaps formed as intermediate products.[2] The quantity of acid used must be sufficient to carry the oxidation through these intermediate steps and then dissolve the resulting disulfide. As the acid becomes more and more dilute, the oxidizing and dissolving power gradually decreases. This fact probably accounts for the ineffectiveness of the 53 Bé. acid.

The fuming and 66 Bé. acids oxidize hydrogen sulfide to free sulfur, in which form it is left in the naphtha. The effect of the 53 Bé. acid could not be accurately checked because the acid was apparently too dilute to oxidize the hydrogen sulfide which the subsequent alkaline wash would remove.

Dimethyl sulfate, methyl *p*-toluenesulfonate, *n*-butyl sulfide, *n*-propyl disulfide, thiophene, diphenyl sulfoxide, and *n*-butyl sulfone were removed by the fuming and 66 Bé. acids. The thiophene was removed as thiophenesulfonic acid, while the others were dissolved apparently unchanged. These results would indicate that, while concentrated sulfuric acid is a sufficiently strong oxidizing agent to convert the mercaptan to the disulfide and to convert hydrogen sulfide to free sulfur, it is not strong enough to oxidize naphtha solutions of any of the alkyl sulfides to the sulfoxide or to the sulfone. The oxidizing reaction of sulfuric acid is as follows:



The 53 Bé. acid removed most of the alkyl sulfate, sulfoxide, and sulfone, but had little effect on the others.

These results indicate that the desulfurizing power of sulfuric acid is a factor of its concentration. The dilute acid is not an effective desulfurizing agent. It also appears that a cracked distillate containing appreciable quantities of hydrogen sulfide should be subjected to an alkali wash prior to an acid treatment; otherwise free sulfur, a corrosive substance, is introduced into the naphtha. Free sulfur may be removed from a distillate by redistillation or by treatment with an alkaline lead mercaptide solution as suggested by Wendt and Diggs.[3] The prior treatment with alkali would also remove some of the mercaptans which would be an additional advantage for the acid treatment.

Table II—Average Per cent of Sulfur in Naphtha Treated with 10 Per cent Sodium Hydroxide Solution

Naphtha Solution	NaOH Solution 4 cc.	NaOH Solution 16 cc.
Free sulfur	0.26	0.26
Isoamyl mercaptan	0.20	0.17
Hydrogen sulfide	0.00	0.00
Dimethyl sulfate	0.03	0.00
Methyl *p*-toluene sulfonate	0.15	0.15
Carbon disulfide	0.08	0.08
n-Butyl sulfide	0.29	0.29
n-Propyl disulfide	0.38	0.38
Thiophene	0.09	0.09
Diphenyl sulfoxide	0.05	0.04
n-Butyl sulfone	0.08	0.08

Effect of Sodium Hydroxide

These experiments were carried out in the previously described closed system using sodium hydroxide of two strengths, 10 and 0.05 per cent. In carrying out the experiments, 50 cc. of each stock solution were treated for 1 hour with 4 cc. and 16 cc. quantities of each strength of alkali. The treated naphtha was then washed with water to remove the excess of alkali and the per cent of sulfur determined. (Table II)

The results from these experiments indicate that the alkali had no effect on free sulfur, methyl *p*-toluene sulfonate, car-

[3] This Journal, 16, 1113 (1924).

Effects of Refining Agents on Naphtha Solutions of Sulfur and Sulfur Compounds

Naphtha Solution	Desulfurizing Sulfuric Acid: Fuming	66 Bé.	53 Bé.	Na_2PbO_2	Na_2PbO_2 + S	NaOH	Silica Gel	Fuller's Earth	Al_2O_3
Free sulfur	None	None	None	None	None	None	None	None	None
Isoamyl mercaptan	Removes as disulfides	Removes as disulfides	None	Removes partially as lead mercaptides	Forms naphtha solution of disulfides	Removes partially as sodium mercaptides	Removes fairly well	None	Removes sparingly
Hydrogen sulfide	Forms naphtha solution of free sulfur	Forms naphtha solution of free sulfur	No oxidation to free sulfur	Removes as PbS	Removes as PbS	Removes as Na_2S	None	None	Removes sparingly
Dimethyl sulfate	Removes readily	Removes readily	Removes fairly well	Removes as $PbSO_4$	Removes as $PbSO_4$	Removes as Na_2SO_4	Removes	Removes	Removes sparingly
Methyl *p*-toluenesulfonate	Removes readily	Removes fairly well	None	None	None	None	Removes fairly well		
Carbon disulfide	None	None	None	None	None	None	None	None	None
n-Butyl sulfide	Removes readily	Removes	None	None	None	None	Removes partially	None	None
n-Propyl disulfide	Removes readily	Removes fairly well	None	None	None	None	Removes partially	Removes sparingly	None
Thiophene	Removes as thiophenesulfonic acid	Removes as thiophenesulfonic acid	None	None	None	None	None	None	None
Diphenyl sulfoxide	Removes readily	Removes	Removes fairly well	None	None	None	Removes	Removes	Removes sparingly
n-Butyl sulfone	Removes readily	Removes	Removes fairly well	None	None	None	Removes	Removes	Removes sparingly

bon disulfide, alkyl sulfide, alkyl disulfide, thiophene, sulfoxide, and sulfone. Both strengths of alkali effectively removed the hydrogen sulfide as Na_2S. The alkyl sulfate was completely removed by the 10 per cent solution and was partially removed by the 0.05 per cent solution as Na_2SO_4. Sixteen cubic centimeters of the 10 per cent alkali removed about 50 per cent of the mercaptan as sodium mercaptide. Sixteen cubic centimeters of the 0.05 per cent alkali solution removed about 25 per cent of the mercaptan. These facts probably explain why it is best to subject a cracked distillate of high sulfur content to an alkali wash or to a sodium plumbite treatment before using sulfuric acid. Severe cracking of a petroleum distillate containing sulfur yields hydrogen sulfide as the final product. However, in actual cracking operations it is probable that hydrogen sulfide is formed along with free sulfur, mercaptans, and other sulfur compounds. If an alkali treatment is employed with a distillate of this character, hydrogen sulfide will be completely and mercaptans partially removed. If sodium plumbite is used, hydrogen sulfide will be completely removed as lead sulfide and mercaptans will be transformed to the corresponding alkyl disulfides, provided enough free sulfur is in solution to react with the resulting lead mercaptide. If the free sulfur is not sufficient for this purpose, the necessary quantity of flowers of sulfur should be added. It is evident that either the alkali or sodium plumbite treatment will render more effective a subsequent acid treatment with a distillate of this character, since sulfuric acid does not remove sulfur when present as hydrogen sulfide and removes mercaptans, as previously indicated, with some difficulty.

Effect of Sodium Plumbite

The sodium plumbite solution used in these experiments was prepared according to directions in *Technical Paper* **298**, U. S. Bureau of Mines. Carefully checked quantitative experiments were carried out in the closed system by treating 50 cc. of each stock solution with 4 and 16 cc. quantities of sodium plumbite solution for 1 hour at room temperature. The recovered naphtha was washed with water and the per cent of sulfur determined.

These results indicate that at room temperature the sodium plumbite solution had no effect on free sulfur, methyl *p*-toluenesulfonate, carbon disulfide, alkyl sulfide, alkyl disulfide, thiophene, sulfoxide, and sulfone. The addition of flowers of sulfur proportionately increased the sulfur content of the naphtha in every case.

The sodium plumbite removed the alkyl sulfate as $PbSO_4$ and the hydrogen sulfide as PbS. The addition of flowers of sulfur is unnecessary and only serves to increase the sulfur content of the naphtha.

The reaction of naphtha solutions of mercaptans with sodium plumbite and flowers of sulfur has been explained by Wendt and Diggs[3] and by Wood, Lowy, and Faragher.[2]

Effect of Silica Gel, Fuller's Earth, and Aluminium Oxide

The silica gel was used as received. The fuller's earth came from Gadsen County, Florida, and was preheated for 2 hours at 250° C. The aluminium oxide was preheated for 3 hours at 1000° C.

Since the degree of fineness, porosity, and heat treatment are vital factors which affect the desulfurizing properties of these materials, the results should not be considered as indicating desulfurizing efficiencies, but rather as indicating the types of sulfur compounds likely to be most affected.

The experiments were carried out in the closed system in the usual manner using 4 grams of each material with 50 cc. of each stock solution for 1 hour at room temperature. The naphtha was recovered without washing and the sulfur content determined.

Table III—Average Per cent of Sulfur in Naphtha Treated with Silica Gel, Fuller's Earth, and Aluminium Oxide

Stock Solution	Silica gel	Fuller's earth	Aluminium oxide
Free sulfur	0.24	0.25	0.25
Isoamyl mercaptan	0.09	0.28	0.24
Hydrogen sulfide	0.03	0.03	0.03
Dimethyl sulfate	0.00	0.00	0.03
Methyl *p*-toluenesulfonate	0.03	0.05	0.15
Carbon disulfide	0.08	0.08	0.08
n-Butyl sulfide	0.13	0.29	0.30
n-Propyl disulfide	0.24	0.32	0.36
Thiophene	0.08	0.08	0.09
Diphenyl sulfoxide	0.00	0.00	0.05
n-Butyl sulfone	0.00	0.00	0.07

The results shown in Table III indicate that silica gel is, in general, a more effective desulfurizing agent than fuller's earth or aluminium oxide. The silica gel completely removed the alkyl sulfate, sulfoxide, and sulfone, removed about 75 per cent of the mercaptan and the methyl *p*-toluenesulfonate, and removed smaller percentages of some of the others. The fuller's earth completely removed the alkyl sulfate, sulfoxide, and sulfone, and partially removed the methyl *p*-toluenesulfonate, but had little effect on the others. Aluminium oxide partially removed mercaptans and the alkyl sulfate, but had little effect on the other sulfur compounds. The action in all cases seems to be due to adsorption. Free sulfur, hydrogen sulfide, carbon disulfide, and thiophene were apparently not affected by any of these materials. In all these experiments it should be kept in mind that the sulfur was in the liquid phase at room temperature and was shaken with the material in a closed system, rather than filtered through it as is frequently the custom.

The sweetening action usually attributed to silica gel is probably due to the ease with which it adsorbs mercaptans.

Arsenic in 1925

The production and sales of arsenic in the United States in 1925 nearly equaled the large output of 1924, according to Victor C. Heikes, of the Bureau of Mines. Four companies that produced white arsenic in the United States in 1925, the American Smelting and Refining Company, United States Smelting, Refining and Mining Company, Anaconda Copper Mining Company, and the Jardine Mining Company, reported sales which amounted to about 12,000 short tons which sold at from 3 to 6 cents a pound. The quantity sold is nearly equal to the total white arsenic produced. About 8000 tons were reported in stock at the end of the year.

During 1925 about 9000 tons of white arsenic were imported into the United States, as shown by actual figures for ten months and an estimate for the remainder of the year. Over 1000 tons of white arsenic were imported in January and in June. Most of the imported white arsenic came from Mexico and from ports in Germany and lesser amounts from Canada, Japan, and Southern Rhodesia. The total available white arsenic in the United States during 1925 therefore amounted to about 29,000 short tons.

Most of the white arsenic was used in the manufacture of insecticides and for weed-killer. Very little calcium arsenate was manufactured for controlling boll weevil during 1925, as the ravages of that pest had far less effect on this year's cotton crop than on previous crops. The manufacturers of weed-killer used about 4 pounds of white arsenic to the gallon of solution, of which over a million gallons were sold.

The price of white arsenic in 1925, as quoted in journals published in New York City, ranged from $5^3/_4$ cents in January, $4^3/_4$ cents in July, $3^3/_4$ cents in September, and $3^1/_4$ cents a pound in December, with only an occasional carload being sold.

Manganese and Plant Growth[1]

By J. S. McHargue

Agricultural Experiment Station, Lexington, Ky.

The old idea that the ten elements, carbon, hydrogen, oxygen, nitrogen, phosphorus, potassium, calcium, magnesium, sulfur, and iron, are the only ones that have important functions in the growth of plants is no longer tenable. Small amounts of the elements manganese, copper, zinc, boron, barium, strontium, iodine, and arsenic are normal constituents in the ash of plants grown under natural conditions in fertile soils in Kentucky. Manganese is as widely distributed in soils and plants as iron, though less abundantly.

When attempts are made to grow plants in purified sand cultures from which manganese has been carefully excluded and in which pure compounds of the so-called ten essential elements are present in available form, plants make no further growth after the food material stored in the seeds has been exhausted. The addition of a small amount of an available compound of manganese to other purified sand cultures containing like amounts of the so-called essential elements will cause plants to grow in a normal way. Manganese functions in the synthesis of chlorophyll and carbon assimilation.

A RESEARCH problem of fundamental importance in the science of agriculture is to ascertain which of the elements that occur in small amounts in plants and animals are necessary and what are their functions.

Hitherto it has been taught and accepted in a general way that only ten elements are necessary for the growth and normal maturation of agricultural crops. In the meantime it has been a well-known fact among agricultural chemists that a considerably greater number of elements than ten occur in small amounts in fertile soils and in the ashes of plants that have grown under natural conditions from the soil. The elements which have been regarded, until recent years, as the only ones essential for the growth of plants are carbon, hydrogen, oxygen, nitrogen, phosphorus, potassium, calcium, magnesium, sulfur, and iron. In the early days of the agricultural chemist and plant physiologist it was quite natural that the elements occurring in the largest amounts in plants should receive first consideration from the standpoint of the plant's economy. However, with the development of new and more delicate methods of chemical analysis and with greater refinement in methods of research, it is not unreasonable to expect that a considerable number of the elements which have been regarded as nonessential for the growth of plants may prove to be very important factors in the metabolism of both plants and animals.

As early as 1840 Justus von Liebig,[2] a pioneer in agricultural chemistry, taught that plants might absorb anything soluble from the soil, but they excreted through their roots whatever was not essential. Moreover, he says the fact that an element is constantly present in any species of plant is sufficient evidence of its necessity.

Abderhalden,[3] in discussing the importance of inorganic foods in their relation to animal metabolism, concludes as follows:

> The more recent investigations concerning the action of the separate salts make it seem most probable that our knowledge concerning the part that inorganic substances play in the metabolism of the cells will shortly be widened greatly, and that before long the inorganic substances in our food will be the subject of considerably more interest corresponding to their importance.

For some time the writer has been interested in the occurrence, distribution, and probable function of a few of the so-called nonessential elements as they occur in plants and animals that have received their sustenance in a natural way from soils in different parts of Kentucky. In this paper will be given a brief résumé of the results thus far obtained in regard to the part played by manganese in the growth of plants.

Historical Part

Manganese is as widely distributed in nature as iron, though much less abundantly. Previous to 1774 compounds of this element were confused with those of iron. In that year Scheele[4] showed that pyrolusite is the oxide of a new and altogether different metal from iron. Scheele conveyed information of his discovery to Gahn, a friend and a contemporary who was a skilful metallurgist, and Gahn isolated the metal a short time thereafter. Scheele proved that manganese is a constituent of rocks and soils and that it is assimilated by plants that grow in the soil, though apparently he made no effort to determine if manganese performs a useful function in the economy of plants.

In 1864, ninety years after Scheele had shown that plants assimilate manganese compounds when grown in the soil, Sachs[5] proved that it cannot replace the function of iron in the growth of plants. However, he failed to show that manganese is also necessary for the growth of plants when iron is available.

In 1883, Yoshida,[6] a Japanese chemist, isolated from the sap of the lac tree a product having peculiar enzymatic properties which he was unable to explain.

About ten years later, 1894, Bertrand[7] repeated the experiment of Yoshida on the sap of the lac tree, determined the chemical composition of the product which possesses the peculiar enzymatic properties, and found that the ash of this material contains 2.5 per cent of manganese. Bertrand named this substance "laccase." He found that laccase is present in varying proportions in the green leaves of different species of plants. After conducting researches for some time on the occurrence of manganese in plants he arrived at the following conclusion: It seems probable that manganese, which exists in small quantities in living organisms, has important functions that have hitherto been unrecognized, probably because the proportion of the element usually present is so minute.

In 1914 Brenchley[8] published the results of an investigation on the effect of manganese sulfate on the growth of barley seedlings in water cultures. She found that with a concentration of 0.00001 of manganese sulfate, or less, a decided stimulation in the growth of the plants was produced; with greater concentrations toxic effects resulted. In her conclusions with respect to the function of manganese in plants she says: "It seems probable that manganese may prove to be an element essential to the economy of plant life, even though the quantity usually found in plants is very small."

From the conclusions drawn by Bertrand and Brenchley, each of whom made important contributions to the subject, it is evident that they were convinced that manganese had some important function in the growth of plants; yet they

[1] Presented as a part of the Symposium on Chemistry and Plant Life before the joint session of the Divisions of Agricultural and Food Chemistry and Biological Chemistry at the 70th Meeting of the American Chemical Society, Los Angeles, Calif., August 3 to 8, 1925.

[2] "Chemistry in Its Application to Agriculture and Physiology."

[3] "Textbook of Physiological Chemistry," 1908, p. 407.

[4] Opuscula Chemica et Physica, Vol. I, 1788. Leipzig.

[5] Handbuch der Experimental-Physiologie der Pflanzen, Bd. IX, 1865, Leipzig, Hofmeister Handbuch der Physiologischen Botanik, Bd. IV.

[6] *J. Chem. Soc. (London)*, **43**, 472 (1883).

[7] *Compt. rend.*, **124**, 1032 (1897).

[8] "Inorganic Plant Poisons and Stimulants," p. 85. Cambridge University Press.

abandoned the subject without having obtained the necessary proof to establish this fact.

In 1914 the author[9] published a paper in which it was shown that manganese is localized in the pericarp of a number of different species of seeds. Further work on the manganese content of different parts of seeds shows that the germs of seeds contain even more manganese than the pericarp. In a few seeds the manganese content is as much as the iron content, but the average for manganese in several different species of seeds is less than that of iron.

After demonstrating the fact that manganese is localized in the pericarp and germs of mature seeds in a very interesting way, the question suggested itself—what would be the ultimate effect on the growth of plants if normal seeds

Spinach in Sand Cultures
Left, Manganese Excluded. Right, Manganese Added

were planted and allowed to grow in a suitable medium which contained adequate amounts of pure compounds of the ten essential elements but from which manganese was withheld? Accordingly, experiments were planned to determine if manganese is an essential element in the growth of plants.

Difficulties Encountered

The best criterion for determining whether an element is essential for plant growth is to show that plants will not grow to maturity in a suitable medium from which the element in question can be shown to be absent during the experiment. In the case of manganese, this degree of security cannot be attained at the outset, for the following reasons: First, the seeds of plants contain enough manganese to maintain a normal growth in plants for about six seeks, when the other ten elements are present in normal amounts. In many of the experiments with water cultures the plants have not been allowed to grow for a sufficient length of time to exhaust the manganese contained in the seeds from which the plants grew; therefore, a negative conclusion concerning the importance of this element in the growth of plants was reached.

Another reason why experiments with water cultures have failed to determine clearly the necessity of manganese as a plant nutrient is the contamination with minute quantities of manganese of the chemical compounds used for plant nutrients. The average chemist probably is not aware that the compounds of calcium, magnesium, phosphorus, and iron which are commonly used as plant nutrients are almost invariably contaminated with small amounts of manganese. In fact, it is difficult to obtain manganese-free chemicals for plant nutrients from dealers in chemicals and upon specification. This is particularly true of iron, calcium, and magnesium compounds. Therefore, manganese contamination of chemical compounds used as plant nutrients undoubtedly has been a source of error to plant physiologists in work carried on for the purpose of testing the necessity of manganese for plant growth.

Another source of error may be the vessel in which the plants are grown. The red earthenware flowerpot and the straight-walled earthenware jars which are carried in stock by grocery stores are in common use for pot experiments. Langenbeck[10] states that all earthenware pots have a varying degree of porosity. He says that even when the walls of an earthenware pot are so hard as not to be scratched with a hard steel point, they will absorb with avidity as much as 15 to 20 per cent of their volume of water, and that even vitreous bodies that were brittle and had a conchoidal, glassy fracture were found to absorb 1.8 per cent of their weight, or nearly 4 per cent of their volume, of distilled water. It is therefore apparent that the walls of earthenware jars which are in general use for pot experiments may be sufficiently porous to absorb mineral nutrients from soil or sand cultures, and these may become available and affect the growth of plants in subsequent experiments. Undoubtedly, many complexities and erroneous conclusions have resulted from the continuous use of the ordinary earthenware jars in pot experiments.

The foregoing errors of technic must be avoided for trustworthy research and it is because such precautions have not been taken by investigators in the past that the important function of manganese in the growth of plants has not been so clearly revealed at a previous time.

Method

Since manganese is so widely distributed in nature it is not an easy task to prepare a solid medium free from this element, which will be suitable for growing plants under conditions that will be as nearly comparable with those of a natural soil as is possible to attain. No such medium occurs in nature; therefore, it is necessary to prepare one from the best material obtainable. Pure quartz sand of fine grain,

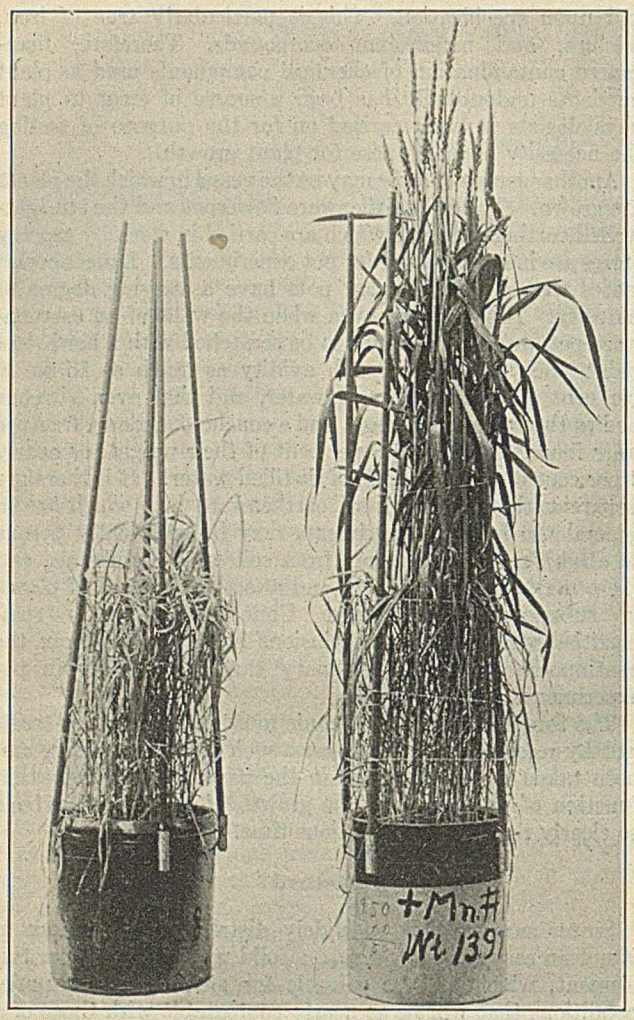
Lettuce in Sand Cultures
Left, Manganese Excluded. Right, Manganese Added

from which all the adhering mineral matter with which the grains are coated in the natural condition, offers the best possibilities for compounding synthetic sand cultures of a definite composition.

After considerable prospecting and examination of a good many samples of sand from different sources, a deposit was located at Erin, Tenn., which was better adapted for purification than others previously examined. This deposit was remarkably free from colored grains and pebbles which most

[9] *J. Am. Chem. Soc.*, **36**, 2533 (1914).

[10] "The Chemistry of Pottery," 1895, p. 48. Chemical Publishing Co., Easton, Pa.



Wheat in Sand Cultures
Left, Manganese Excluded. Right, Manganese Added

ordinary deposits of sand contain. A sufficient supply of the natural deposit was obtained and the dry sand was run through a 10-mesh sieve to remove fragments of undecomposed sandstone and such other extraneous matter as could be removed in this way. The clay and fine silt were removed by washing the sand in running water and a uniform grade of yellow grains of quartz sand was thus obtained. To remove the yellow coating of iron oxide, which also carried manganese, the sand was digested in large porcelain dishes over boiling water with a mixture of hydrochloric and nitric acids, washed with clear tap water until the acids were removed, and finally rinsed with distilled water; upon drying, snow-white sand composed of grains of quartz was obtained.

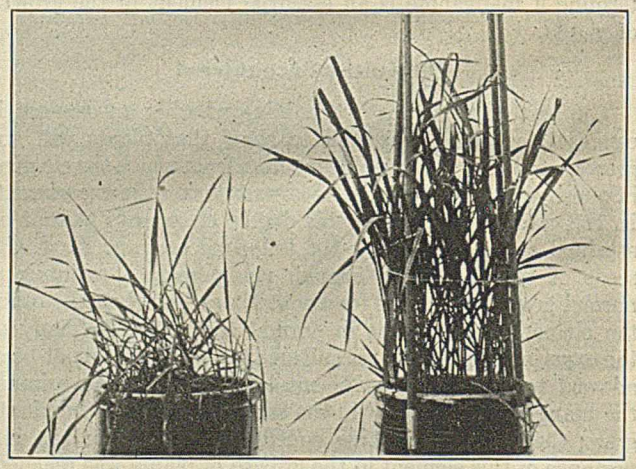
Two-gallon acid-proof stoneware jars were made upon a special order. These pots are well glazed and not subject to absorbing mineral nutrients in the way that ordinary, cheaper types of pots do.

The necessary number of pure chemical compounds that were tested and shown to be free from manganese, having been obtained for the plant nutrients, synthetic sand cultures were prepared by thoroughly mixing with 8000-gram portions of the purified quartz sand the following amounts of the manganese-free plant nutrients: 25 grams of calcium carbonate ($CaCO_3$), 10 grams of dipotassium hydrogen phosphate (K_2HPO_4), 10 grams of calcium nitrate ($Ca(NO_3)_2.4H_2O$), 5 grams of magnesium sulfate ($MgSO_4.7H_2O$), 3 grams of potassium nitrate (KNO_3), 2 grams of potassium chloride (KCl), and 2 grams of iron in the form of hydrous ferric oxide ($Fe_2(OH)_6$). Each 8000 grams of sand with the plant nutrients, after thoroughly mixing by hand in a large porcelain dish, was transferred to a clean, acid-proof stoneware jar, the individual weight of which had been recorded. Half the pots were reserved for the check experiments—that is, the cultures from which manganese was excluded as nearly as possible. To the other pots 2 grams of manganese carbonate ($MnCO_3$) were added and mixed thoroughly with the sand containing the other mineral nutrients. Sufficient distilled water to bring the moisture content to about three-fourths saturation of the sand was added to each pot and the weight recorded. A definite number of selected seeds of the several species of plants with which experiments were to be made were planted in each of the pots, and after the plants were up and at the proper size they were thinned to the same number of normal plants to each pot. When the plants needed watering, enough distilled water was added to each pot to restore the original weight.

Thus far in the investigation corn, wheat, oats, soy beans, cow peas, garden peas, garden beans, tomatoes, onions, cucumbers, spinach, and lettuce have been grown in purified sand cultures with and without the addition of manganese under the conditions described above and with very striking results, some of which are shown in the accompanying photographs.

Discussion

One of the first signs of the lack of manganese in the growth of plants is the failure of these plants to synthesize chlorophyll; the young leaves and branches as they put forth are chlorotic and do not attain a normal green color. The parts of the plants that have become chlorotic die and little if any further growth is made. If the plants that have developed the chlorotic conditions because of the lack of manganese are treated with an available compound of this element, they can be revived and brought back to a normal color and growth, if taken in time. Furthermore, it has been shown by qualitative tests that the starch and sugar content of the leaves



Oats in Sand Cultures
Left, Manganese Excluded. Right, Manganese Added

of plants that became chlorotic because of the lack of manganese is much less than the starch and sugar content of similar leaves of other plants of the same species that were grown during the same time in sand cultures containing manganese, all other conditions being the same.

These facts show that manganese is an important and necessary factor in the synthesis of chlorophyll and carbon assimilation. Experiments not reported herein tend to show that no other one of the more common elements,

including iron, copper, zinc, boron, or arsenic, will replace this function of manganese in the growth of plants. Heretofore it has been thought that iron alone is chiefly concerned in the synthesis of chlorophyll. From the writer's results and observations he is led to conclude that manganese plays a role of importance equal to that of iron in the synthesis of chlorophyll and that both these elements are indispensable for the formation of chlorophyll and the growth of plants. Manganese occurs in the largest concentrations in the leaves and the pericarp and germs of seeds of plants.

California Petroleum Insecticides[1]

Laboratory and Field Tests

By G. P. Gray and E. R. de Ong

California Department of Agriculture, Sacramento, Calif., and University of California, Berkeley, Calif.

Laboratory and field tests were made of about thirty-five petroleum distillates to determine to what extent, if any, the various physical tests are significant in determining the toxicity of an oil to vegetation. It was concluded that physical tests alone are inadequate.

The toxicity of the oils tested appeared to increase roughly in proportion to the amount of unsaturated compounds present. A sulfonation test (the percentage of the oil soluble in 37 *N* sulfuric acid) may be used to estimate the amount of unsaturated compounds in an oil and is suggested as a useful guide in judging toxicity. The ability of an oil to penetrate plant tissue must also be taken into account.

PETROLEUM oils and their derivatives are toxic to insects to a marked degree and stand well towards the head of the list of the important classes of insecticides. These oils are so varied in character that it has been possible to collect an assortment of products with properties favorable for use in the control of many kinds of insects and under a wide range of conditions.

The lighter and more volatile distillates, such as benzine and gasoline, have properties desirable for the control of a number of the household pests. The less volatile kerosene, a refined and highly standardized distillate from this source, has long occupied an important place in spray practice. More recently the crude petroleums themselves, as well as a great variety of unrefined and nonstandardized distillates therefrom, have come into extended use as insecticides. Certain of these have proved to be cheap and effective materials for both dormant and foliage sprays, for the control of parasites of animals and for the control of mosquitoes and other disease-bearing insects in the interest of public health. Experience has shown that, although many of these unrefined and consequently cheaper materials are considerably more toxic to insects than kerosene, they are also more toxic to vegetation. The use of petroleums and their derivatives on plants may be attended with little or no injurious effect, but on the other hand, many cases of grave consequences following their use are on record. Mature maple trees have been killed by the application of a distillate spray during the dormant period. Citrus orchards have been partially defoliated following the use of distillate sprays. Similarly, the major part of the season's crop of fruit has at times been caused to drop to the ground, and very often a considerable percentage of fruit has been rendered unsalable or greatly lessened in market value.

Injurious results following the application of these oils to dormant trees are comparatively rare, although of a very serious nature when they do occur. Deleterious effects on fruit and foliage of plants, however, following the use of unrefined petroleum distillates are of such frequent occurrence and are so often very serious that this particular phase of the matter was considered of the most immediate importance for investigation.

The selection of a suitable insecticide from this great variety of products of the oil refiners is a difficult matter. The habits and susceptibility of each particular insect must be taken into consideration, as well as the nature of the host whether it be plant, animal, the furnishings of dwellings, the clothing of man, etc. To decide all these matters, practically the only test commonly employed by the user of these oils as insecticides is that of density, usually expressed in degrees of the Baumé scale. The flash point of an oil has been suggested for use in conjunction with the Baumé test. The common belief among entomologists is that an oil with a high specific gravity and an abnormally low flash point is very injurious. That these tests are inadequate for the prediction of the performance of an oil in the field is a matter of common knowledge. The experiments were outlined to determine to what extent, if any, the various tests were significant in indicating the suitability of an oil for use as an insecticide.

One gallon samples were collected of petroleum distillates which were thought to be representative of these materials in use as insecticides throughout the state. These samples were then examined in the laboratory, applying the more important methods which may be found in textbooks.[2] The action of the oils on foliage was later observed, with the results reported in the latter part of the paper.

These experiments were commenced in 1915 and continued through the summer of 1916. Unfortunately, it became necessary to discontinue the investigation at that time, and the matter was laid aside in the hope of taking it up later. Meanwhile, the senior writer resigned from the staff of the California Agricultural Experiment Station and the data secured and conclusions have never been published. This paper is presented not as a finished piece of work, but with the idea that some of the data may be of interest to other experimenters and suggest further investigation of the relation of the composition of petroleum oils and their usefulness as insecticides.

[1] Presented as part of the Insecticide and Fungicide Symposium before the joint session of the Divisions of Agricultural and Food Chemistry and Biological Chemistry at the 70th Meeting of the American Chemical Society, Los Angeles, Calif., August 3 to 8, 1925.

[2] Hamor and Padgett, "The Examination of Petroleum," 1920, and others.

Methods of Examination

Methods of examination commonly employed by refineries and consumers are principally physical tests rather than chemical. Tests have been devised for gasoline to determine its burning qualities and its ability to run an automobile satisfactorily. Kerosenes are examined to determine their illuminating power, their freedom from smoke-producing constituents, and the presence of highly volatile substances. The viscosity is of much importance in the examination of lubricating oils. These and other tests are of value for their respective purposes, but it is doubtful whether they have much significance in the examination of an oil to determine its usefulness in the control of insects. Some of the more common tests will be reviewed and their significance explained.

Density—The density or specific gravity of an oil (commonly expressed in degrees Baumé) is important and indicates to some extent the nature of an oil, whether thick or thin. This test is applied to all oils, and serves as the first clue by which the nature of a crude is judged as well as the standard by which the various fractions are "cut" in the process of distillation. Petroleum oils of the same density may vary within wide limits in volatility and other important characteristics. This test does not disclose the actual constitution of an oil nor can it be relied upon to determine the adaptability of an oil for any purpose. Lighter and heavier oils may be mixed in different proportions to obtain any density between that of the original oils. Even unblended oils of the same density but from different sources often have very different characteristics.

Flash Point—This is the lowest temperature to which the oil must be heated to give off vapor in sufficient quantity to produce a combustible mixture with air. This test is an indication of the presence of volatile constituents and of their relative volatility. An abnormally low flash point may indicate the blending of a light and a heavy oil or may be taken as a suspicion of the presence of hydrocarbons of the aromatic series. The most important information to be obtained from a determination of the flash point of kerosene is in regard to the safety of the oil.

Distillation—Valuable information may be obtained concerning the nature of an oil by distilling it and noting the quantity and density of the fractions distilling between ranges of temperatures at stated intervals. The commercial value of crudes can be determined in this way—that is, the percentage of gasoline, kerosene, and lubricating oils which they are expected to yield on refining, the most important process of which is distillation and separation of the various fractions. This is probably the most important test which is applied to the various distillates.

Viscosity—The viscosity or freedom of motion of the molecules of an oil, often spoken of as "body" or "fluidity," is an important property in the selection of a lubricating oil. This property is often expressed as the rate of flow through a definite orifice at a standard temperature in comparison with that of water as a standard. The apparatus used to determine viscosity reported in the table is known as the Stormer Viscosimeter, and compares the rate at which a metallic cylinder will revolve in the oil with that in water at the same temperature.

Other Tests

It is unnecessary to describe the technic of these methods of examination, which are all readily accessible in books on the subject. Two other tests were applied to the oils, one of which is not so well known to petroleum chemists and not so widely used, and one which is original with the writers. These will be described in full.

In order better to understand the first test sulfonation, and its possible significance in relation to petroleum insecticides, it seems desirable to say a few words about refining processes.

Refining Processes—Distillation is the fundamental process in the refining of commercial products from the raw crudes. By this means the lighter products are separated from the heavier. The undesirable aromatics and cracked oils are not removed by distillation, however, but must be removed by chemical means.

Sulfuric acid is the reagent commonly employed for this purpose. In fact, it is said that, aside from distillation, the only refining process of general application is the agitation of the oils with sulfuric acid. The odors of gasoline and kerosene are "sweetened" and the lubricating stocks are brought much nearer marketable condition by this treatment. The greater cost of production of the higher refined oils is largely chargeable to refining acid and the loss of the oil removed in the process. These differ from the cheaper grades in the care which has been exercised in their distillation, but the greatest difference appears to be the extent to which they have been refined with sulfuric acid.

The aromatic and cracked oils are chemically active and will unite readily with sulfuric acid to form complex organic substances known as sulfonates. On the other hand, the paraffin[3] hydrocarbons are scarcely affected by treatment with sulfuric acid. These facts constitute the basis of the chief chemical refining process for the petroleum distillates, for the removal of offensive odors, smoky hydrocarbons, and other undesirable constituents. The distillate is agitated with sulfuric acid, which combines with the aromatics and cracked oils, forming sulfonates and liberating sulfur dioxide, which escapes as a gas. When agitation is discontinued, the excess sulfuric acid and sulfonated oils settle to the bottom of the tank and are drawn off from the upper layer of oils, which has not reacted with the acid. The layer which is drawn off and discarded is known as acid sludge, and consists of free acid, a mixture of the sulfonated aromatic oils and cracked oils, and other minor constituents of the original distillate. The upper layer of purified oil consists of paraffin hydrocarbons and as much of the aromatics and olefins as has escaped sulfonation. More than one treatment with acid may be required in the purification of a very foul oil to prepare a marketable product.

Sulfonation Test—The important constituents of a petroleum distillate may be divided into two distinctive classes of oils: (1) chemically inert hydrocarbons of the paraffin series, and (2) chemically active hydrocarbons of the aromatic series and of the olefin series (cracked oils). Both classes of oils, especially the lighter members of the series, are known to be toxic to insects and plants. In selecting oils of equal density from the two classes, for a comparison of their probable toxicity, it appears that those of the second class will be the more toxic for the following reasons: The aromatics and many of the olefins are known to have greater capillarity and less viscosity, and hence greater penetrating qualities than the paraffin hydrocarbons; but the second class has greater chemical activity.

A determination of density, viscosity, capillarity, or other physical characteristics may adequately indicate the extent to which an oil may be expected to penetrate into the tissues of a plant, but in addition to this, some knowledge of the chemical constitution of an oil is needed to be able to predict its toxicity. It therefore seemed desirable to determine quantitatively the proportions of the two classes of oils in refined and unrefined distillates. A test much in use by the refiners is as follows: One hundred cubic centimeters each of the oil and concentrated sulfuric acid are shaken together in a graduated cylinder, cooling from time to time, and cautiously releasing the liberated sulfur dioxide. On standing, two layers will separate, nonreactive oils above and a mixture of the acid and sulfonated oils below.

Although this test gives an approximation to the amount of sulfonatable oils in a distillate, it did not seem to be suffi-

[3] California oils are known to contain other constituents known as naphthenes, which do not react with sulfuric acid.

ciently accurate to meet the requirements. Many hours' shaking was required before the maximum sulfonation occurred. A method perfected by the United States Forest Service[4] for the examination of coal-tar creosotes for adulteration with petroleum oils was found to be quite satisfactory with slight modification. This method is essentially one of sulfonation, using fuming sulfuric acid and heat to hasten the reaction.

Procedure. The exact concentration of fuming and concentrated sulfuric acid is determined by titration. The acids are then mixed in proper proportion to prepare acid exactly 37 *N*. Five cubic centimeters of the oil to be tested are pipetted into a 30 or 50 per cent Babcock cream-test bottle, 10 cc. of the 37 *N* acid added, shaken 2 minutes, 10 cc. more of the acid added, and shaken again 2 minutes. The test bottle is then placed in a water-jacketed oven, kept at a temperature of 95° to 100° C. for 1 hour, during which time it is well shaken every 10 minutes. At the end of the hour the bottle is removed and filled with ordinary sulfuric acid to bring the oil within the graduation of the bottle. After centrifuging 5 minutes, the top layer of unsulfonated oil is read. The reading is multiplied by 4, which gives directly the percentages by volume of the unsulfonated oil. This, subtracted from 100, gives the per cent by volume of the sulfonated oils.

It is quite important to use fuming acid of exactly 37 *N* concentration. If weaker acid is used the sulfonation is incomplete; if stronger, the oils are likely to be charred.

Some of the oils were so viscous that accurate measurement was difficult. Others were so much charred by the acid that a reading of the separated oil was impossible. To overcome these difficulties, a troublesome oil and an oil of known sulfonation value were mixed in equal proportions and 5 cc. of the mixture sulfonated as usual. The sulfonation value of the unknown oil was then calculated from the result by subtracting one-half of the per cent sulfonation of the known oil from the per cent sulfonation of the mixed oils and multiplying the remainder by 2.

Capillarity Test—The viscosity of an oil is supposed to determine to some extent the ability of an oil to penetrate tissue. This cannot always be relied on, as viscosity is not an additive property; that is, the resultant viscosity of two mixed oils is not necessarily an average of that of the original oils. Other tests, therefore, seem necessary to show the ability of an oil to penetrate tissue. At the suggestion of Prof. C. W. Woodworth, the capillarity of the oils was tested on crayon. Ordinary blackboard crayon gave surprisingly uniform results when used as an arbitrary test of the capillarity or penetrating qualities of an oil. A pair of crayons was suspended in the oil to be tested and another pair in distilled water at a temperature equal to that of the oil. At the end of 30 minutes the distances which the crayons were wet above the surface of the liquids were measured. The figures given for capillarity in the table are the ratios of these distances—that is,

$$\frac{\text{Distance for oil}}{\text{Distance for water}}$$

This distance for water was usually between 67 and 68 mm., while that for the oils varied from 1 to 70 mm. Duplicate determinations seldom varied more than 1 mm.

Laboratory Experiments

The laboratory tests were made by both writers in the Insecticide and Fungicide Laboratory at Berkeley, Calif., during the summer of 1916.

Data obtained from examination of the oils are given in the table. The fractions from all the oils distilling between the same temperatures were combined, the portions of the oils distilling between 150° and 175° C. being known as Distillate Fraction 1, those distilling between 175° and 200° C. as Distillate Fraction 2, etc. It was thought that in this way a series of oils of varying density and volatility could be obtained which would represent the average of the oils under examination. The original purpose of this procedure was to determine whether or not any fraction, or group of fractions, is particularly safe or particularly toxic to use. It was thought that the selection of a certain "short-cut oil" might avoid some of the dangers usually encountered. This hope was not realized, however, as indicated by the field tests.

All the data presented in the tables do not have a definite bearing upon the toxicity of the oils. They are given, however, because data of this kind in published literature are very limited and they may prove of interest to experimenters who have to do with petroleum distillates.

Data for gasoline, "crude xylene," chemically pure xylene, and petrolatum are included in the tables for comparison. "Crude xylene" (3605) is an oil said to be recovered from acid sludge or from a crude petroleum naturally rich in aromatic oils. Having about the same density as kerosene, it seemed to be a very good material for comparison with it to determine the effect on plants of an oil of unusually high content of oils soluble in sulfuric acid (45 per cent). In the field tests acute injury occurred whenever this was applied. Xylene is a pure aromatic oil, usually obtained from coal tar.

"Liquid Petrolatum" (2487) is sold as a medicinal oil for intestinal lubrication and is colorless, odorless, and tasteless. It is prepared from California petroleum by an exhaustive refining process, the most important of which is thought to be treatment with sulfuric acid. This sample furnished a highly refined heavy oil for comparison with other heavy oils of high content of acid-soluble oils. The sample was not obtained in time for tests at Riverside, but the tests at Berkeley placed this oil at the bottom of the list as the least injurious (see table). The low solubility of this oil in sulfuric acid, 1 per cent, is significant in this respect.

Field Experiments

The field tests were made by the junior writer, those at the Citrus Experiment Station at Riverside, during the summer of 1915, in coöperation with Prof. H. J. Quayle, entomologist of that station.

A block of three-year-old navel and Valencia orange trees was set aside for experimental use at the Citrus Experiment Station at Riverside. These trees were cultivated and irrigated as often as necessary to promote their normal growth. Unfortunately, the effect of the oil could not be determined on the fruit, as these trees had not yet come into bearing.

The oils were emulsified by means of soap powder, the amount being uniform throughout all the experiments. As little of the soap powder was used as possible so as to minimize the effect of the emulsifying agent. The sprays were applied with a bucket spray pump to one side of the tree only, so that the opposite half would serve for comparison. The experiments were repeated wholly or in part two or more times, with similar results.

The composite distillate fractions were chosen for the basic experiment, as more was known of their history than of any oils which could be obtained in the open market. Furthermore, they had been "cut" within narrower limits of temperature at intervals of 25° C. The lighter oils were applied in emulsions ranging from 20 to 5 per cent of oils, this being both above and below the strength used in orchard practice. The heavier oils were applied at a range of 5

[4] Bateman, *U. S. Dept. Agr., Forest Service, Circ.* **191** (1911).

Tests of California Petroleum Insecticides

		Laboratory Tests								Field Tests			
											Types of Injury Produced		
											Defoliation		
Sample	Sold as:	Density 16° C. (60° F.) Sp. gr.	° Bé	Flash point ° F.	° C.	Viscosity 20° C.	(Stormer) 25° C.	Sulfonation Per cent soluble in 37N H_2SO_4	Capillarity on crayon in 30 min. Water = 1	Order of toxicity to plants	In 5% emulsion Per cent	In 10% emulsion Per cent	Other Injury
3622	Distillate	0.914	23.2	109	42.8	2.198	1.877	46	0.326	1	50		Nature fruit injured
3610	No. 2 distillate	0.955	16.6	336	169.0	47.589	36.400	71–87	0.030	2	20		Bearing wood stunted
3605	"Crude Xylene" (not a commercial material)	0.825	39.6	57	13.3	0.905		45	0.918	3			Very severe leaf spotting
D.F. 10	Large residue undistilled at 325° C.	0.927	20.9	348	176.0	5.406	4.001	44	0.262	4	18		Tips of limbs stunted
D.F. 7	Composite fraction distilling between 300° and 325° C.	0.891	27.0	219	104.0	1.354	1.310	32	0.322	5	18		Tips of limbs stunted
3626	Distillate	0.906	24.5	115	46.1	1.769		40	0.251	6	15		Leaves turned very yellow
D.F. 6	Composite fraction distilling between 275° and 300° C.	0.880	29.1	180	82.0	1.239	1.202	26	0.406	7	7		Leaves turned very yellow
3611	Subdistillate	0.918	22.4	183	84.0	2.657		46	0.173	8	4		Leaves turned yellow
3612	Dark neutral	0.920	22.2	275	135.0	3.654		40	0.094	9	4		Leaves turned yellow
3613	Gas oil	0.887	27.7	205	96.1	1.484		28	0.338	10	4		Leaves turned yellow
3624	Distillate	0.884	28.4	165	73.9	1.269		32	0.296	11	3	10	
3193	Stove distillate	0.870	30.9	102	38.9	1.228		22	0.476	12	2	10	
3599	Distillate, 27°–29° Bé.	0.881	28.8	159	70.5	1.161		24	0.405	13	2	8	
D.F. 5	Composite fraction distilling between 250° and 275° C.	0.868	31.3	158	70.0	1.195	1.083	23	0.481	14	2	7	
3625	Distillate	0.868	31.2	125	51.6	1.141		28	0.470	15	2	6	
3614	No. 1 distillate	0.837	37.3	101	38.3	1.044		22	0.639	16	1	4	
3191	Stove distillate 32°–34° Bé.	0.855	33.6	122	50.0	1.159		21	0.566	17	0	2	
3627	Distillate	0.842	36.3	98	36.6	1.013		20	0.622	18	0	2	
3195	Stove distillate	0.849	34.9	99	37.2	1.082		20	0.648	19	0	1	
3594	Stove distillate	0.853	34.0	125	51.6	1.071		18	0.722	20	0	1	
D.F. 4	Composite fraction distilling between 225° and 250° C.	0.852	34.3	118	48.0	1.070	0.998	22	0.602	21	0	1	
3190	Stove distillate, 38.5° Bé.	0.829	38.9	97	36.1	1.027		17	0.761	22	0	½	
3609	Kerosene	0.823	40.1	102	38.8	1.025		16	0.738	23	0	0	
3600	Distillate, 36°–38° Bé.	0.836	37.3	77	25.0	1.017		20	0.729	24	0	0	
D.F. 3	Composite fraction distilling between 200° and 225° C.	0.835	37.7	99	37.0		0.901	18	0.678	25	0	0	
D.F. 2	Composite fraction distilling between 175° and 200° C.	0.815	41.8	81	27.0		0.899	17	0.765	26	0	0	
D.F. 1	Composite fraction distilling between 150° and 175° C.	0.797	45.7	70	21.0		0.854	16	0.844	27	0	0	
3662	"Pearl Oil"	0.812	42.4	104	40.0	0.961		9	0.696	28	0	0	
2487	"Liquid Petrolatum Squibb (Heavy)"	0.891	27.1	397	203.0	11.000		1		29	0	0	
D.F. 8	Single fraction distilling between 325° and 350° C.	0.889	27.4					34	0.288				
D.F. 9	Small residue undistilled at 325° C.							54	0.135				
2488	"Tree Distillate"	0.853	34.0	143	61.6	1.035		23	0.723				
2489	"Crude Kerosene" (water-white stock)	0.823	40.0	96	35.5	0.981	0.977	17	0.862				
3623	Xylene, C. P.	0.865	31.7	Room temperature		0.881			1.210				
3663	Gasoline	0.740	59.0	Room temperature		0.846			1.086				

Order of toxicity to plants: Very toxic (1–6); Moderately toxic (7–16); Comparatively safe (17–22); Safe (23–29); Not determined (D.F. 8, D.F. 9, 2488, 2489, 3623, 3663).

to 1.25 per cent of oils, their great insecticidal power making them effective at these percentages. A common basis for all the oils used was 5 per cent. In addition to the laboratory samples a few typical commercial oils were included, such as kerosene, gasoline, and a sample which contained a large amount of aromatic oils and referred to in the table as "crude xylene" (3605) for convenience. This is said to be an oil recovered from acid sludge. Sample 3610, a very heavy lubricating oil, was also included in this experiment for comparison with other heavy oils.

The effect on the trees was noted from time to time over a period of 65 days. The action of the undiluted oils in some of the experiments was typical, kerosene having very little immediate effect when applied to the foliage, but if allowed to come in contact with the roots severe injury resulted. Gasoline and "crude xylene" always caused severe burning of both the leaves and wood.

The kerosene type of oils (39° to 42° Bé.), when used at double the customary 10 per cent strength, had no bad effect on foliage, which indicates a wide margin of safety for this group. With an increase in gravity to 34° Bé., there occurred a slight defoliation at 10 per cent (which is about twice as strong as this oil is commonly used), showing a narrower range of safety for these oils than the previous ones.

As the gravity increased injury was nearly always more marked, even though the percentage of oil was reduced to 1 or 2 per cent. Oils ranging from 25° to 35° Bé., when applied in excessive strengths, caused defoliation ranging from 1 to 100 per cent. In using the heavier distillates there was very little immediate change in the appearance of the leaves, but at the end of the second day after application the leaves began dropping and continued until the fourth or fifth day. The bearing wood which had been defoliated appeared stunted, new growth was slow in starting, and when the foliage did appear it was often weak. The tree threw out a thick, vigorous growth of sprouts around the base of the defoliated limb, indicating a severe disturbance of the normal functions of the sprayed branches. Such a condition sometimes lasted for a period of a week up to several months.

Very heavy oils, 15° to 22° Bé., had a slower action than those of a lighter character. Defoliation was not so common but the leaves had a greasy appearance and turned yellow after a few days, indicating some action on the chlorophyll. There was little, if any, new growth for weeks or months after the application of the oil, but less tendency to sprout at the base of the limbs than was found with lighter oil.

Three rather distinct types of injury to the foliage and branches were observed: (1) killing the leaf tissue within 48 hours after applying, as with gasoline, C. P. xylene, and "crude xylene;" (2) defoliation, the leaves dropping off at the end of 3 or 4 days, but without losing color to a marked degree, and a stunting of the bearing wood; (3) a deposit

of oil on the leaves, accompanied by a decided yellowing and a stunting effect of all sprayed parts, which appears 2 or 3 weeks after the application of the oil and may be present for months.

Comparison of the notes in August with those made in June showed that injury by light oils was not permanent unless from excessive dosages or when the roots were weak. Severe defoliation, common with heavy oils, was accompanied by chronic effects such as yellowing of the foliage, stunting of the bearing wood, the sprouting in the center of the tree, and the production of stunted leaves to replace those lost.

Experiments at Berkeley

A second series of experiments was carried on in the summer of 1916 at Berkeley, Calif., on citrus trees, black walnut, and wild morning glory (*Convolvulus arvensis*). This work, being in a much cooler and more humid climate and on different plants, served as a check on the Riverside experiments.

The results from the application of oil emulsions to citrus trees were similar to those recorded at Riverside, but on walnut and morning glory were quite different, since these plants are more susceptible to injury by oil and for this reason showed differences more accurately, especially in the light oils. For example, Distillate Fractions 1, 2, and 3 gave practically the same results on orange, but a marked difference was seen when applied to morning glory. The action was also quicker and more intense than on hardier foliage. The action of the heavy oil, No. 3610, on this plant was similar in effect to the results obtained at Riverside—viz., a slow acting chronic effect, beginning with yellowing and resulting in death of the leaf tissue. No. 3662 was a highly refined kerosene sold under the trade name of "Pearl Oil." Its use on the tender morning glory foliage emphasized strikingly the safety of this oil over the less refined kerosenes tested, for at 10 per cent, the common strength for insecticidal purposes, no damage had resulted at the end of 6 days, while on walnut there was no injury even at 20 per cent at the end of 6 days.

Interpretation of Laboratory and Field Data

A summary of the action of oils on foliage is shown in the table. The 5 per cent emulsion was taken as a basis for the arrangement according to toxicity to plants, as this was the common strength at which all the oils were used. It was found necessary to include also the results from 10 per cent emulsions to bring out more closely the difference in toxicity of those approaching the kerosene type. These data are based largely on the results of the experiments on citrus trees, as this is the most complete of any of the sets. When necessary the effect of the oils on morning glory plants was taken into consideration in order to differentiate the action of the less toxic oils. As far as possible the oils are listed in order of toxicity to plants. This, however, was a very difficult matter, as more than one type of injury must be considered, as well as seasonal variations, the condition of the plant, errors in compounding, etc. There was some doubt about the proper order of arrangement of many of the oils. No difficulty was experienced, however, in deciding to place the first four oils at the head of the list as the most injurious, and Samples 3662 and 2487 at the bottom as the least injurious. The oils may be divided into four groups according to their toxicity to plants, as shown in the table. Careful inspection of the data shows that none of the tests are infallible in determining with certainty the group to which on oil belongs. The density and sulfonation tests, however, appear to be of the most value. Other tests, such as viscosity and capillarity, may also be of use, but these matters need much more study before their full significance can be determined. The significance of what appear to be the two most important tests will be discussed below.

Density—The specific gravity (commercially expressed in degrees Baumé) may be taken as a fairly reliable index of the toxicity of a normal oil direct from the still—a fraction or "cut" which has not been blended to change its gravity, or otherwise manipulated, by refining processes or sophistication. From the field tests of the composite distillate fractions (the averages of the "cuts" at 25-degree intervals of all the samples collected) it was evident that their toxicity increased quite uniformly as the specific gravity increased. If, however, the aromatics and the cracked oils have been largely removed by treatment with sulfuric acid or otherwise, a heavy oil may be quite harmless when applied to plants (Sample 2487). In this case the Baumé test would have been entirely misleading. Furthermore, a case of more practical interest is well illustrated by referring to Sample 3605. This oil has the specific gravity of a kerosene and in the absence of other tests would have been considered a comparatively harmless oil. This oil and the C. P. xylene (3623) were probably the most active of any of those tested in producing acute foliage injury.

Sample 3622, testing 23° Bé., would doubtless have been rejected as being too heavy for use on foliage, but one would not suspect it completely to defoliate the trees on the south side and injure great quantities of mature fruit when applied in an emulsion at the rate of 6 gallons to a 220-gallon tank. This, however, is the commercial record of this distillate when used on a 10-acre orange grove in southern California. Its classification as the most toxic oil is based upon its actual record when applied commercially. The quantitative distillation of this sample, and other tests, make it appear to be a blend of light and heavy oils.

It is concluded that the specific gravity of a petroleum distillate is of service in determining the probable toxicity of the oil to plants, provided the distillate is direct from the still without further treatment, and is not from a crude unusually high in aromatics or from a still designed to crack the oils under pressure. In conjunction with the specific gravity, an abnormally low flash point may be taken as a suspicion of the presence of aromatics or cracked oils.

It is concluded that a determination of the specific gravity of a petroleum distillate will be of little service in detecting a very toxic oil under the following conditions:

(1) A blend of a light oil low in aromatics and cracked oils, and a heavier oil high in aromatics and cracked oils
(2) A distillate from a crude high in aromatics
(3) A product composed wholly or in part of oils recovered from acid sludge
(4) A distillate from a still designed to crack the oils under pressure

Sulfonation Test—The laboratory and field data have been carefully reviewed in relation to the significance of the sulfonation test in predicting the relative toxicity of a petroleum distillate. The test has been applied to a great many oils not listed in the tables, and the performance of the oils under actual working conditions has been followed. During the progress of an investigation by the senior writer on the destruction of noxious weeds by means of chemicals, sulfuric acid-soluble oils have been shown to be very effective as herbicides. An oil recovered from acid sludge appeared to be as effective as sodium arsenite in the control of several weeds. Green leaves and grasses withered and turned brown in less than an hour after its application, and were dry enough to burn readily within 24 hours.

With very few exceptions, these observations pointed toward the conclusion that the constituents which are capable of being removed from a petroleum distillate by re-

fining with sulfuric acid are the most toxic to foliage. The sulfonation test, therefore, seems to offer the most reliable test of the probable toxicity of a petroleum distillate of any of the methods of examination thus far tried. All the oils of the first group, classified as very toxic to plants, contain large percentages of chemically active oils (sulfuric acid-soluble), seven of them containing over 40 per cent; the average of the second group is less; the average of the third group is still less; and the average of the fourth group, the safe oils, is the least.

The sulfonation test is, therefore, proposed as a laboratory method for the examination of petroleum distillates for the estimation of their degree of refinement, and their probable toxicity to foliage.

Subjection of Molasses Treated with Zeolites to the Steffens Process[1]

By F. R. Bachler

American Beet Sugar Co., Oxnard, Calif.

A short résumé is given of the efforts, described in the literature, to introduce natural and artificial zeolites into the sugar industry.

The causes of past failures are recalled; a new angle of the subject is presented by the author, who subjects molasses not treated and treated with zeolites to the Steffens process.

Procedure is described in detail, and analyses are given that seem to support the author's viewpoint that molasses freed of its potash contents with the help of zeolites gives superior results when subjected to Steffens process.

FOLLOWING a series of experiments made by the author to determine the technical and commercial possibilities of removing and recovering potash from beet molasses with the help of natural and artificial zeolites, the question arose as to how a beet molasses thus treated would respond to desugarization by the Steffens process.

The base-exchanging power of zeolites, so successfully and widely applied in the softening of water where it is desired to replace calcium and magnesium salts with those of sodium, can under proper conditions be also applied in replacing the various sodium and potassium salts of sugar solutions with the corresponding lime salts.

The first observations in this direction were made by Rümpler,[2] who established the fact that the potassium and sodium contents of sugar-beet thin juices were greatly reduced if they were allowed to percolate through layers of certain clays. Rümpler[3] later found that this phenomenon was due to the action of zeolites. He proved that sugar solutions thus treated were purified to a certain extent. Some large-scale experiments were made in several German sugar factories, but the results were unsatisfactory owing to the low exchange power of the zeolites employed.

Later, after success in producing a synthetic zeolite of high exchange power, Gans[4] used his artificial product, Permutite, anew to solve the problem of removing potassium salts from beet sugar solutions. His Permutite had the approximate composition of SiO_2 34.00, Al_2O_3 25.00, Na_2O 14.75, and H_2O 25.40 per cent. By treating this material with a calcium chloride solution he converted it into a calcium permutite, "which contained but little Na_2O." Gans concentrated his efforts on the purification of beet thin and thick juice because he agreed with Rümpler that the purification of a sugar solution should logically be attempted in the first stages of the manufacturing process in order to increase the yield of crystallized sugar by reducing the quantity of melassogenic nonsugars.

Laboratory experiments with thin and thick juices were highly successful and promised greatly to advance the art of making sugar. In the same year Claassen[5] critically reviewed the work of Rümpler and Gans and admitted that a considerable exchange of bases had taken place, but that these juices, now greatly enriched by calcium salts, not only possessed a far greater viscosity than the untreated juices but that concentration of treated juices to the point of crystallization became almost impossible owing to the presence of these lime salts. Investigation of the problem by others, including small-sized factory tests, confirmed Claassen's view.

Theory

All attempts in the past to apply zeolites to the purification of sugar solutions centered on the treatment of beet thin and thick juices. By treating molasses with zeolites prior to subjection to the Steffens desugarization process, the author is guided by the thought that the resulting base-exchange reactions will not only change the character of the molasses but influence its behavior, sugar yield, etc., during the Steffens desugarization.

Obviously the removal of all or a large part of the sodium and potassium salts will influence the purity of the molasses. By "purity" in sugar factory terminology is meant the per cent sugar contained in the dry substance of a sugar product, the interpretation of the term being the higher the purity the greater the value of the product because of the greater yield of crystallized sugar obtainable therefrom. This point of view must, therefore, not be overlooked when judging the value of a purification process.

One may also expect that the removal of sodium and potassium will cause profound chemical changes due to the setting free of the acid radicals with which sodium and potassium in the molasses are combined. It is a fact that all the alkali salts of a molasses are soluble. When treating a molasses with a calcium zeolite it is possible that the liberated acid radical may combine with the calcium set free from the zeolite, to form an insoluble calcium salt. Such a reaction would, of course, be a step in the right direction, that

[1] Received August 12, 1925.

[2] *Deut. Zuckerind.*, **26**, 585, 625 (1901).

[3] *Z. Ver. deut. Zuckerind.*, **53**, 798 (1903).

[4] *Ibid.*, **57**, 206 (1907).

[5] *Z. Ver. deut. Zuckerind.*, **57**, 931 (1907).

Table I—Comparison of Original Molasses with Zeolite-Treated Molasses

A—Original molasses as used for all experiments
B—Same molasses after diluting preparatory to Steffens process but before zeolite treatment
C—Same as B, but after zeolite treatment. Solutions B and C were filtered prior to analysis

Item		Solution A As found Per cent	Solution A On dry substance Per cent	Solution B As found Per cent	Solution B On dry substance Per cent	Solution C As found Per cent	Solution C On dry substance Per cent
1	Moisture	14.20		86.57		87.98	
2	Dry substance	85.80	100.00	13.69	100.00	12.23	100.00
3	Dry substance by refractometer	87.72	102.23	13.99	102.19	12.50	102.20
4	Dry substance by Brix spindle	92.40[a]	107.69	14.55	106.28	12.86	105.15
5	Direct polarization	48.20	56.18	7.70	56.24	7.65	62.55
6	Clerget polarization	48.96	57.06	7.82	57.12	7.75	63.36
7	Carbonate ash	10.40	12.12	1.665	12.16	1.608	13.14
8	Sulfate ash + 10 per cent	12.07	14.07	1.922	14.04	1.832	14.98
9	Total nonsugars referred to dry substance, Clerget polarization, and carbonate ash	26.44	30.82	4.205	30.72	2.872	23.50
10	Organic nonsugar by difference	16.04	18.70	2.540	18.56	1.264	10.36
11	Nonsugar coefficient $= \frac{\text{Clerget polarization}}{\text{Total nonsugar}}$	1.85		1.86		2.70	
12	Saline coefficient $= \frac{\text{Clerget polarization}}{\text{Carbonate ash}}$	4.71		4.70		4.82	
13	Organic coefficient $= \frac{\text{Clerget polarization}}{\text{Organic nonsugar}}$	3.05		3.07		6.13	
14	Impurity coefficient $= \frac{\text{Total nonsugar}}{\text{Clerget polarization}} \times 100$	54.00		53.77		37.05	
15	Inorganic coefficient $= \frac{\text{Carbonate ash}}{\text{Clerget polarization}} \times 100$	21.24		21.29		20.74	
16	Impurity coefficient − inorganic coefficient, by difference	32.76		32.48		16.31	
	Determination of Carbonate Ash						
17	$Fe_2O_3 + Al_2O_3$			0.008	0.06	0.013	0.105
18	Ca			0.021	0.15	0.463	3.785
19	Mg			0.007	0.05	0.018	0.146
20	K			0.560	4.09	0.008	0.066
21	Na			0.222	1.62	0.173	1.416
22	SO_4			0.153	1.12	0.147	1.201
23	Cl			0.184	1.35	0.172	1.410
24	PO_4			0.008	0.06	0.007	0.058
25	CO_3			0.513	3.75	0.627	5.124
26	Total			1.676	12.25	1.628	13.311

[a] On double-diluted molasses.

of diminution of nonsugars, which is equivalent to a proportionate rise in purity.

According to Lippman,[6] the potassium salts of the numerous organic acids occurring in molasses form, with a part of the sugar of the molasses, alkali saccharates, which he describes as viscous, sirupy, water-soluble, and very stable compounds. Some sugar technologists maintain that it is the presence in the molasses of these alkali saccharates which prevents complete precipitation of the molasses sugar by the lime treatment of the Steffens process.

From a consideration of these premises it may reasonably be expected that the removal from the molasses of all, or a very large part, of its sodium and potassium contents will reduce the sum total of the melassogenic nonsugars by substituting an insoluble calcium salt for a part of the soluble alkali salts. It is also reasonable to infer that an increase in yield of sugar due to steffenizing zeolite-treated molasses may occur, owing to the partial or complete elimination of the alkali saccharates.

Experimental

It is not intended to enter at this time into a description and discussion of the mechanism of removing alkali salts from molasses with zeolites. This part of the work and description of method of recovery of the potash liberated by zeolite treatment of molasses form part of a study as yet uncompleted. The subject under discussion refers exclusively to comparisons of results obtained by steffenizing untreated and zeolite-treated molasses.

Table I presents a series of analyses that are typical of the conditions after successful treatment of molasses with suitable zeolite. Solution B clouded slightly after preparation, but filtration through paper resulted in a clear filtrate; the residue consisted almost entirely of organic matter. Solution C turned decidedly cloudy after standing a little while, but upon filtration through paper a clear filtrate resulted, the dry residue from 100 grams of filtrate weighed 0.194 gram; ignition left 0.046 gram of ash consisting almost entirely of lime.

A comparison of analyses of zeolite-treated and untreated molasses solutions and their ashes is interesting. Purity of treated molasses rises from 57.12 to 63.36 per cent (Item 6), showing that a real purification has taken place. This purification must be due to the removal of organic and inorganic nonsugars. Item 9 shows that the total nonsugars decreased from 30.72 per cent in the untreated molasses to 23.5 per cent in the treated molasses. This decrease is due solely to the reduction of organic nonsugars (Item 10), which fell from 18.56 per cent in the untreated to 10.36 per cent in the treated molasses. The ash of the treated molasses is about 1 per cent higher than that of the untreated molasses. These facts find a more impressive expression in the various coefficients (Items 11 to 16).

In the ash analyses the outstanding features of the zeolite-treated molasses are a greatly increased calcium and an equally remarkable decrease of the potassium contents, the latter amounting to 98.3 per cent of the potash originally present, while the sodium content decreased but 12.5 per cent.

Solutions B and C were subjected to desugarization according to Steffen. In order to give strictly comparable results both solutions were diluted to exactly 6.5 per cent polarization, which concentration is also considered good factory practice. After cooling both solutions in an ice bath to 10° C., 110 per cent CaO in form of a powder, of which 99.6 per cent passed through a 200-mesh screen, was added. This addition was made slowly and under constant stirring to avoid a rise in temperature above 15° C. Immediately following the addition of the lime the mass was filtered through a Büchner funnel under vacuum. Each precipitate, in factory terminology called "cold saccharate," was washed with 200 cc. of ice-cold water. The wash water was allowed to

[6] "Die Chemie der Zuckerarten," 1895, p. 755.

mix with the original mother liquor ("cold waste water"). The cold saccharate was weighed, tested for CaO and sugar, and then set aside for further analyses. The mixed cold waste water and wash water were weighed, CaO and sugar determined, and then gradually heated to 85° C. for the purpose of precipitating part of the sugar contained therein in the form of "hot saccharate." The heated mixture was filtered under vacuum through a hot water-jacketed Büchner funnel, the hot saccharate cake obtained was washed with 100 cc. of hot distilled water and again the wash water was allowed to mix with the mother liquor, the combined liquids representing what is called in factory operations "Steffens waste to sewer." The hot saccharate cake was weighed, tested for CaO and sugar, and then combined with cold saccharate cake. The "Steffens waste to sewer" was weighed, CaO, sugar, and alkalinity determined, and then discarded. The combined cold and hot saccharate cakes of each lot separately were mixed with water, heated, carbonated, filtered; the filter residue was washed with hot water and discarded. The filtrate was evaporated under vacuum to sirup density, again filtered and analyzed. The results obtained are shown in Tables II and III.

Table II—Comparison of Results of Steffenizing Molasses before and after Zeolite Treatment

Item		Solution B	Solution C
	Cooler Solution		
1	Weight of cooler solution taken, grams	10,000	10,000
	Analysis:		
2	Dry substance, per cent	11.56	10.39
3	Polarization, per cent	6.50	6.50
4	Purity, per cent	56.24	62.55
5	Weight of sucrose, grams	650.0	650.0
6	CaO content of lime powder, per cent	98.2	98.2
7	Per cent CaO on sucrose (5)	110.00	110.0
8	Weight of CaO necessary, grams	715	715
9	Weight of lime powder taken, grams	728	728
	Cold Saccharate		
10	Weight of cold saccharate produced, grams	3400	3789
11	Sucrose, per cent	16.4	15.4
12	Weight of sucrose, grams	557.6	583.5
13	Sucrose recovered in per cent on (5)	85.79	89.77
14	CaO (total alkalinity expressed as CaO), per cent	17.5	16.2
15	Per cent CaO on 100 sugar	106.7	105.2
16	Weight of CaO in grams	595.0	613.8
17	CaO recovered in per cent on (8)	83.2	85.8
	Mixed Cold Waste and Wash Water		
18	Weight of mixed cold waste and wash water, grams	7519	7128
19	Weight of sucrose calculated by difference (5−12), grams	92.4	66.5
20	Calculated per cent sucrose in waste water	1.23	0.93
21	Per cent sucrose by polarization	1.16	0.96
22	Weight of CaO in waste water calculated by difference (8−16), grams	120.0	101.2
23	CaO in waste water as calculated, per cent	1.59	1.41
24	Total alkalinity expressed as CaO, per cent	1.89	1.48
25	CaO as determined gravimetrically, per cent	1.64	1.50
	Hot Saccharate		
26	Weight of hot saccharate produced, grams	434	343
27	Per cent sucrose	11.1	12.7
28	Weight of sucrose	48.2	43.5
29	Sucrose recovered in per cent on (5)	7.41	6.69
30	Per cent CaO (total alkalinity expressed as CaO)	9.42	10.6
31	Per cent CaO on 100 sugar	84.8	83.2
32	Weight of CaO, grams	40.9	36.2
33	CaO recovered in per cent on (8)	5.72	5.06
	Hot Waste and Wash Water		
34	Weight of hot waste and wash water, grams	7072	6780
35	Weight of sucrose, calculated from difference (5−12 + 28), grams	44.2	23.0
36	Calculated per cent sucrose	0.625	0.339
37	Per cent sucrose by polarization	0.56	0.39
38	Weight of CaO calculated by difference [8−(16 + 32)], grams	79.1	65.0
39	Per cent CaO as calculated	1.12	0.96
40	Total alkalinity expressed as CaO	1.64	1.05
41	Per cent CaO as determined gravimetrically	1.03	1.00
	Recapitulation		
42	Weight of sucrose recovered in cold and hot saccharates, grams	605.8	627.0
43	Per cent of total sucrose recovered ("Steffen extraction") on (5)	93.2	96.46
44	Weight of CaO recovered in cold and hot saccharates, grams	635.9	649.8
45	Per cent CaO in 100 sugar in hot and cold saccharates	104.9	103.6
46	Per cent CaO recovered in both saccharates in per cent on (8)	88.9	90.8

Table III—Analyses of Sirup Resulting from the Evaporation of Carbonate Juices of Combined Hot and Cold Saccharates

	Solution B As found Per cent	Solution B On dry substance Per cent	Solution C As found Per cent	Solution C On dry substance Per cent
Moisture	44.44		48.16	
Dry substance	55.56	100.00	51.84	100.00
Dry substance by refractometer	56.74	102.12	52.66	101.58
Dry substance Brix spindle	57.6	103.67	53.58	103.36
Direct polarization	48.35	87.02	45.65	88.05
Clerget polarization	48.24	86.82	45.71	88.17
Apparent purity from Brix and direct polarization	83.95		85.2	
Carbonate ash	2.26	4.07	2.43	4.69
Sulfate ash + 10 per cent	2.34	4.21	2.55	4.92
Total nonsugars referred to dry substance Clerget polarization and carbonate ash	5.06	9.11	3.70	7.14
Organic nonsugar by difference	2.80	5.04	1.27	2.45
Alkalinity as CaO	0.058	0.104	0.053	0.102
Lime salts by titration with soap solution	0.410	0.737	0.486	0.937
Color degrees according to Stammer	18.6	33.47	13.1	25.27
Nonsugar coeff. $= \frac{\text{Clerget polarization}}{\text{Total nonsugars}}$	9.53		12.35	
Saline coeff. $= \frac{\text{Clerget polarization}}{\text{Carbonate ash}}$	21.34		18.81	
Organic coeff. $= \frac{\text{Clerget polarization}}{\text{Organic nonsugar}}$	17.22		36.00	

The analytical results given in Tables I and III point to the conclusion that zeolite-treated molasses subjected to the Steffens process yields a higher recovery of sugar and saccharates of superior quality than is the case with the same molasses not treated with zeolite.

Interesting alkalinity relations are found to exist in the various waste waters: Total alkalinity of the waste waters of the untreated molasses is in each instance considerably higher than that of the waste waters from the treated molasses, the latter figure agreeing closely with the CaO of all waste waters determined gravimetrically. This difference must be due to the presence of potassium in the waste waters of the untreated molasses. This fact and the fact that the waste water from the untreated molasses contains considerably more sugar than that of the treated molasses lend support to the supposition that alkali saccharates exist in the untreated molasses which do not break up when subjecting to the Steffens process.

Cement Company Breaks Safety Records

All safety records during its quarter of a century's history were broken last year by the Universal Portland Cement Company, according to the president, B. F. Affleck, who stated:

While production greatly increased during the last 25 years, the accident rate has steadily declined until last year it was only a fraction of 1 per cent in relation to the total number of persons employed. In our plant at Duluth, for example, the whole year passed without having an hour's time lost on account of accidents. Our plants in other cities produced similarly good results.

During the month of December just finished a 100 per cent safety record was achieved at all our plants, no time being lost anywhere because of accidents. The significance of this record is revealed when one recalls that thousands of men are employed day and night operating burning, crushing and grinding machinery, elevators, conveyors, cranes, packing machines and electrical apparatus required in making some 60 million sacks of cement in a year.

Mr. Affleck named two factors as being chiefly responsible:

Modern mechanical safeguards to protect workers in hazardous circumstances are installed wherever needed. This naturally tends to reduce risks to employees who may be careless.

But no machine can be 100 per cent guarded. There always must exist personal responsibility on the part of the worker. We find therefore that the most effective means to secure safety is to talk safety, to teach it, and to educate employees always to think of it. Hence there are safety meetings conducted in various languages; there is literature distributed that features safety; there are printed placards urging workers to be careful; there are prizes for mills and groups who make the best records. Through these means there is developed individual caution and a sense of pride in preventing accidents that have done much to make industry safe.

A Portable Combustion Apparatus for Detection and Measurement of Small Quantities of Petroleum Vapor[1]

By C. A. Neusbaum, P. L. DeVerter, and E. W. Dean

STANDARD OIL COMPANY (NEW JERSEY), STANDARD INSPECTION LABORATORY, NEW YORK, N. Y.

An outline of the relative merits of various types of apparatus used for detecting and estimating small percentages of petroleum vapor follows a brief discussion of the requirements of the work of inspecting ship tanks.

A convenient and accurate portable apparatus which reduces these disadvantages to a minimum, and which has been developed and used by the authors, is described.

ONE of the frequent technical problems involved in the operation of oil-tank vessels is the testing of the atmosphere of tanks and compartments when a ship is to be sent to dry-dock for repairs. There are various methods of doing this, but none of them have been found entirely satisfactory by the authors. As a result of experience in inspecting ships of the tank fleet of this company, apparatus and procedure have been developed which seem to meet all the requirements of this work. They are probably applicable, also, to the testing of oil tanks other than those of ships, but the authors have confined their discussion to marine problems because their experience has been entirely in this field.

General Requirements of Ship Tank Inspection[2]

It seems desirable first to point out one or two fundamental principles that apparently are not universally recognized. The first is that no inspector can write a real certificate of safety unless he has himself entered the tank or compartment in question and examined it carefully for deposits of oil or sediment that may generate vapor. Without such an examination the analysis of the atmosphere means nothing more than that the tank is safe for a man to enter at the time of testing. The practice of taking samples by lowering a sampling tube into the container seems entirely inadequate.

Another important principle is that the maximum permissible content of petroleum vapor is fixed by its effect on men inhaling the atmosphere rather than by the lower limit of the explosive range. The lower explosive limit varies with different hydrocarbons, but 2 per cent is, perhaps, a representative figure. On the other hand, it is stated[3] that petroleum vapors, in concentrations of 0.3 per cent or more, are intoxicating to some people on exposure for 30 minutes or longer; so the actual danger limit is far below the explosive limit. The authors have found that men were able to work in tanks for periods considerably in excess of 30 minutes when a maximum of 0.2 per cent of petroleum vapor, figured as pentane, was enforced as a limit, and have adopted this figure for their inspection work.

The third fundamental is a practical one. The working time of a ship is very valuable and any delays in her movement cause the loss of considerable sums of money. It is therefore desirable to make an inspection rapidly and to have the results available for sending to the master in the shortest possible time.

Failure of Older Methods to Satisfy These Requirements

The best method previously available consists in collecting an adequate set of samples, making a careful physical inspection at the same time, and analyzing these samples in the Haldane apparatus.[4]

The Haldane apparatus is accurate and reliable, but at best the analysis of the samples consumes much time and it is necessary to take the samples from the ship to the laboratory, frequently a considerable distance. In spite of these defects it was believed that the importance of the work warranted employment of this method until apparatus was devised that made greater speed possible without sacrifice of accuracy.

Other types of nonportable apparatus are available, some requiring less skilful manipulation than the Haldane apparatus, but none are appreciably more rapid than the latter when it is used according to an abbreviated procedure involving simple determination of the contraction after combustion.

The Burrell methane detector has been employed for the determination of small quantities of petroleum vapor,[3] and under favorable conditions might prove satisfactory. An attempt was made to use this apparatus, but it was not suitable under the conditions encountered. The temperatures of oil tanks just after they have been steamed and cleaned are decidedly irregular, and to give accurate results the Burrell detector must be approximately in thermal equilibrium with the atmosphere in which it is used. The time consumed in reaching temperature equilibrium in each tank of a ship is prohibitive.

It has recently been proposed to use the Koehler safety lamp[5] as an indicator of the presence of combustible constituents in the atmosphere of tanks. This lamp shows an increase in flame height when it burns in an atmosphere containing combustible gases or vapors, but it is not considered to be reliable in indicating concentrations lower han 0.5 per cent. Its use is undoubtedly preferable to the old-fashioned scheme of relying on odor as an index of content of combustible gas; but it hardly seems justifiable to rely on it for testing tanks prior to turning them over to workmen with the guarantee that they are safe for work with flames, hot rivets, etc.

The N-D Portable Apparatus

The authors' experience therefore indicated that the most practical apparatus would be one which represented a com-

[1] Received September 18, 1925.

[2] The Marine Department of the Standard Oil Company (New Jersey) has issued a pamphlet covering its rules and regulations for this work. A limited supply of copies are available which will be furnished on application to men or organizations interested in work of this nature.

[3] Jones and Yant, *Bur. Mines, Tech. Paper* **352**, 8 (1924).

[4] Jones, *Bur. Mines, Rept.* **299-B-71**; Burrell and Seibert, *Ibid., Bull.* **42** (1913).

[5] Wilson and Wilkin, THIS JOURNAL, **16**, 1154 (1924).

promise between the accuracy and reliability of the Haldane, and the portability of the Burrell detector. Their apparatus, which for purposes of convenient reference has been designated as the "N-D" apparatus, is really a laboratory set, which, however, can be readily transported to a convenient location, such as the cabin of a ship that is to be inspected. It requires careful handling and its operation involves a fair amount of skill and training, but it has served a very useful purpose in making accurate results available in the shortest possible time after a ship is ready for inspection.

Combustion System

A detailed drawing of the apparatus is shown in Figure 1. It consists of a slow combustion chamber, *b*, and buret or measuring tube, *f*, combined in the form of a U-tube.

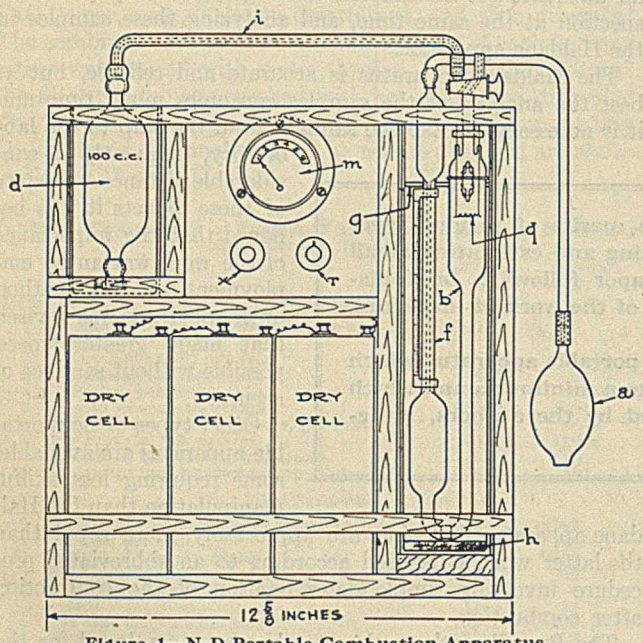


Figure 1—N-D Portable Combustion Apparatus

The ground-joint stopper used in the combustion chamber is held in place by two rubber bands which are stretched over the lugs shown in the figure. The reason for using a ground-glass connection is twofold: (1) The small platinum wire, which may burn out, can be renewed easily and the chamber cleaned by removing the stopper. (2) In case of an explosive mixture or the development of excess pressure, the rubber bands stretch, allowing the stopper to rise, so that the gaseous mixture can escape. This usually prevents breakage of the apparatus.

Mounted on the buret or measuring tube is a scale graduated in millimeters. The use of this scale will be discussed under the section on calibration.

The U-tube is supported by two hard-rubber disks and is immersed in water to insure a constant temperature.

Rheostat

The nichrome wire rheostat, *r*, is used to give a more careful regulation of the temperature of the platinum coil than can be obtained by the batteries alone. An air sample containing a large amount of combustible vapor causes the wire to become very hot, and unless some additional resistance is thrown into the circuit, the wire may be burned out.

Ammeter

The ammeter, *m*, is inserted in the circuit and its reading noted when the desired bright yellow color of the platinum wire, *q*, is observed. Thereafter by adjusting the rheostat the wire may be brought to the same temperature by reference to the ammeter reading rather than by observation of the wire itself, which is frequently made difficult by the cloudiness of the walls of the chamber.

Source of Electric Current

The electric current for heating the platinum wire is supplied by three dry cells or three small two-cell Edison storage batteries. Dry cells have been found most convenient for ship inspection in that new ones can always be supplied from the vessel stores.

Procedure for Analysis

The U-tube, which has previously been filled with mercury until the level in the buret is at 0, is connected with sample tube, *d*, and the stopcock turned so as to put the combustion chamber into communication with the atmosphere. The rubber bulb, *a*, is pressed to force the mercury up to the bottom of the stopcock, which is turned through one-quarter turn so as to hold the mercury. The stopcock is gradually turned making communication between the chamber and sample tube, *d*, at the same time allowing the sample to be drawn in as the mercury seeks its level. This sample is used to clean out the connecting tube, *i*, and the combustion chamber, *b*, by turning the stopcock so as to make communication between the atmosphere and the chamber and pressing the bulb until the mercury level rises to the bottom of the stopcock. A sample is then drawn from the sample tube, *d*. After the sample has been drawn the stopcock is opened to the atmosphere to allow the pressure to equalize. The

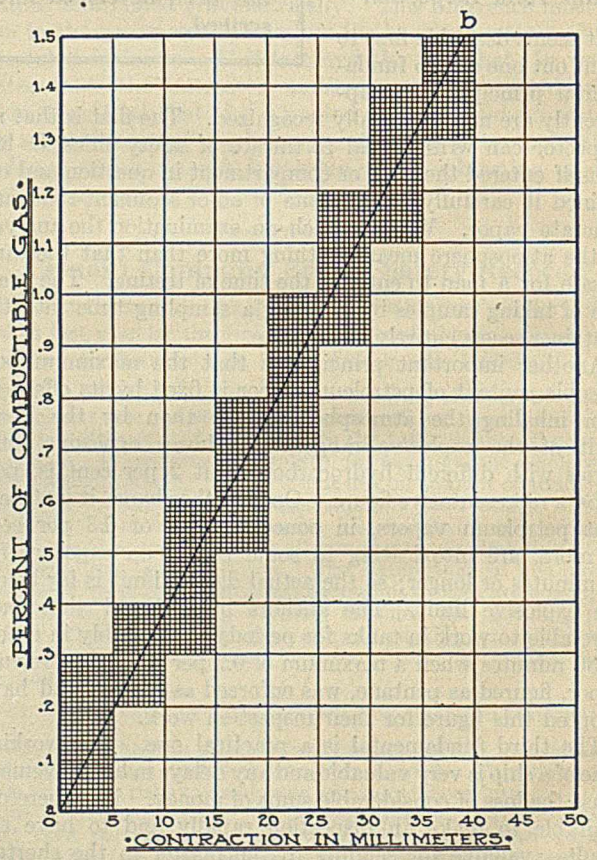


Figure 2—Characteristic Curve for N-D Portable Combustion Apparatus, Based on Pentane

stopcock is closed completely, the reading noted, and, with all the resistance thrown in, the switch, *x*, closed. The resistance is then regulated until the desired reading of the ammeter is obtained. After burning for 2 minutes the cur-

rent is broken and the sample allowed to cool for 3 minutes. After cooling, the contraction in millimeters, indicated on the scale, is read.

PRECAUTIONS—The walls of the buret and combustion chamber should be kept slightly moistened to insure accurate results. Water should be kept above the point at which the platinum wires are sealed into the glass stopper, since any leaks around the stopper or seals can be detected readily.

Calibration of Apparatus

The results obtained by use of the apparatus are empirical and their interpretation involves the use of a calibration table or chart. The fundamental factors involved in working up such a table or chart are ably and fully discussed by Jones and Yant.[3] The chart employed in the present work is similar to those described by Jones and Yant.

The method of calibrating the N-D apparatus has been to prepare mixtures of air with varying proportions of hydrocarbon vapor, and to determine the composition of these mixtures with the Haldane set, figuring the percentages of combustible material on the basis of the chemical equation characteristic of pentane. Portions of the same mixtures were tested in the N-D apparatus and the contractions (in millimeters) determined, which were equivalent to the various percentages of hydrocarbon vapor, calculated as pentane. These figures are used in preparing a chart such as is shown in Figure 2. This chart is used to convert the contraction readings into percentages of combustible vapor.

Another Important Role Played by Enzymes in Bating[1]

By John Arthur Wilson and Henry B. Merrill

A. F. GALLUN & SONS CO., MILWAUKEE, WIS.

During the liming of skin for tanning, keratin is partially broken down into keratose, which is soluble in neutral or alkaline solution, but is precipitated at its isoelectric point, pH = 4.1. If this material is left in the skin and precipitated there by the acid tan liquors, the value of the finished leather is lowered. In bating, keratose is broken down by the enzymes to a point where it is no longer precipitable by acid. The rate of digestion of keratose is directly proportional to the concentration of enzyme and is a maximum at pH = 7.9.

IN MODERN tannery practice, after the skins have been limed, unhaired, scudded, and washed, but before they are tanned, they are subjected to a process called bating, which consists in paddling the skins, still plumped by the alkaline lime liquor, in a warm solution of pancreatin and buffer salts designed to keep the pH value at about 8 until they have been reduced from a plump to a flaccid condition.[2] Bating is an extremely complex process and one which is difficult to operate efficiently at all times. Limed skin, with its manifold and variable protein degradation products, may be acted upon by enzyme bate liquors, with their countless bacteria, in many different ways. Depending upon the kind of skin, its previous treatment, and the kind of leather desired, bating may serve one or more very useful purposes, or it may be without appreciable effect, or it may actually prove harmful. Moreover, where bating is desirable, the method of operation must be varied to correspond with any variations in previous treatment of the skin.

It has been the aim of the writers to ascertain all of the useful purposes which bating may serve, to study the mechanism of the reactions involved, and to devise means for controlling each reaction so that the particular purpose may be served most efficiently. Already five different purposes of bating have been recognized and means for their quantitative control indicated: (1) rendering the skin flaccid; (2) adjusting the hydrogen-ion concentration of the solution adhering to the skin; (3) removal of lime; (4) removal of elastin fibers; and (5) partial digestion of collagen. To these the writers are now adding a sixth, the removal of keratose, and this forms the subject matter of the present paper.

The prevailing opinion has been that the chief function of the enzymes in bating is to digest the elastin fibers of the skin,[3,4,5,6] thus rendering the grain surface of the finished leather finer, softer, and clearer in color, although Röhm and Haas[7] have suggested that probably a more important function consists in dissolving out any remains of unorganized material known as scud, which is derived from the epithelial tissues and is insoluble in neutral or alkaline solution.

Wilson and Daub demonstrated conclusively by means of photomicrographs that the elastin fibers of calfskin can be completely removed by solutions of pancreatin without appreciable damage to the collagen fibers. In fact, the only action of the enzymes in bating which they could detect under the microscope was the removal of the elastin fibers. However, the writers' experience since that time has demonstrated clearly that the beneficial effects of the enzymes in bating are not always measured by their power to digest elastin. If the dissolved keratose which is present in limed skin is not removed before tanning, it will be precipitated in the skin by the acid tan liquors, with consequent damage to the appearance of the grain surface of the leather. The soluble keratose is much more quickly broken down by the enzymes of the bate liquor than the insoluble elastin fibers, and it was found in numerous tests that nearly all measurable effects of the bating of certain types of calfskin were obtained before the elastin fibers had been measurably attacked.

Thus the removal of keratose must be added to the list of important functions of bating, and the following report deals with the quantitative relations involved and with the measurement of the keratose digesting power of bating materials.

Preparation of Keratose

The material in which we are interested consists of those decomposition products of keratin which are soluble in al-

[1] Received October 15, 1925.

[2] For a detailed account of this process see Wilson, "The Chemistry of Leather Manufacture," p. 173.

[3] Rosenthal, *J. Am. Leather Chem. Assoc.*, **11**, 463 (1916).

[4] Krall, *Société Anonyme anc. B. Siegfried*, private bulletin, **1918**.

[5] Seymour-Jones, *J. Soc. Leather Trades' Chem.*, **4**, 60 (1920).

[6] Wilson and Daub, THIS JOURNAL, **13**, 1137 (1921).

[7] *J. Am. Leather Chem. Assoc.*, **18**, 516 (1923).

kaline solution and precipitated upon acidification. The term "keratose" has been limited to this material in consequence of which the keratose content of the prepared solutions may be defined as the weight of material precipitated by the addition of acid to the point of maximum precipitation.

The keratose used in these experiments was prepared by digesting thoroughly cleansed calf hair with ten times its weight of 2 *N* sodium hydroxide for 18 hours at 25° C.

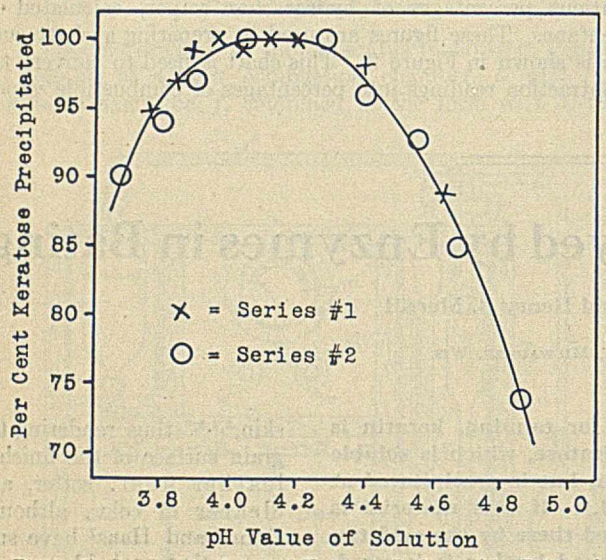


Figure 1—Isoelectric Point of Keratose Indicated by Point of Maximum Precipitation

The resulting solution was treated with hydrochloric acid to reduce the pH value to 8, at which the keratose is still soluble. The solution was filtered and then acidified to pH = 4, at which point the keratose was precipitated as a voluminous, white mass, such as is seen when titrating a used lime liquor with acid. The precipitate was allowed to settle in tall cylinders and washed repeatedly by decantation. Finally, it was redissolved by adding sodium hydroxide to make the pH value of the solution equal 8. This solution was preserved with a small amount of thymol and kept in the refrigerator until used.

Isoelectric Point

The isoelectric point of keratose was measured by the pH value causing maximum precipitation. Keratose solution, containing approximately 2 per cent by weight of keratose, was mixed with an equal volume of the powerful citrate-phosphate-borate buffer solution described by Northrop[8] and 8 volumes of water. One hundred cubic centimeter aliquots were pipetted into 50-cc. portions of acetic acid solutions of different concentrations to give pH values covering the range of maximum precipitation. The precipitate formed in each case was filtered off, dried, and weighed. The maximum amount precipitated in any test was taken as the total keratose content and the percentage precipitation in the other tests was calculated from this. Two entirely independent series of tests were run and both are plotted in Figure 1. The point of maximum precipitation is fairly sharply defined at pH = 4.1. It is believed that this is the first time a figure has been reported for the isoelectric point of keratose.

An attempt was made to cover a greater range than that shown in Figure 1, but at pH values just outside this range the precipitate was so slimy as to be practically unfilterable.

[8] *J. Gen. Physiol.*, **5**, 263 (1923).

At pH values still further removed from the range no precipitate was formed at all. It is rather important to note that the isoelectric point of keratose corresponds closely to the pH value of many tanning solutions.

Experimental Procedure

The immediate object of this investigation was to determine the rate of hydrolysis of keratose by pancreatin as a function of pH value, time, and concentration of both enzyme and keratose. The keratose and enzyme solutions were mixed with Northrop's citrate-phosphate-borate buffer solution to which hydrochloric acid or sodium hydroxide had been added to produce the desired pH value in the digesting mixture. The object of the buffer solution was to maintain constancy of pH value during the digestion, and electrometric measurements made before and after each digestion showed that this was accomplished. It was also demonstrated that the presence of the buffer material did not introduce any complications, since series run without added buffer gave results more erratic, but otherwise similar in value to those obtained with buffer material. The digestions were made at 40° C.

At the end of the digestion period the undigested keratose was precipitated by the addition of enough acetic acid–sodium acetate mixture to bring the pH value to 4.1, filtered off, dried, and weighed on a tared filter paper.

The pancreatin used was from the same parcel as that used and described by Wilson and Daub.[6]

Effect of pH Value

Figure 2 shows how the hydrolysis of keratose varies with pH value in the presence and absence of pancreatin. Subtracting the values in curve *B* from those in curve *A*, we get curve *C*, which represents the extra hydrolysis due to the added enzyme. At pH values below 5.5 and above

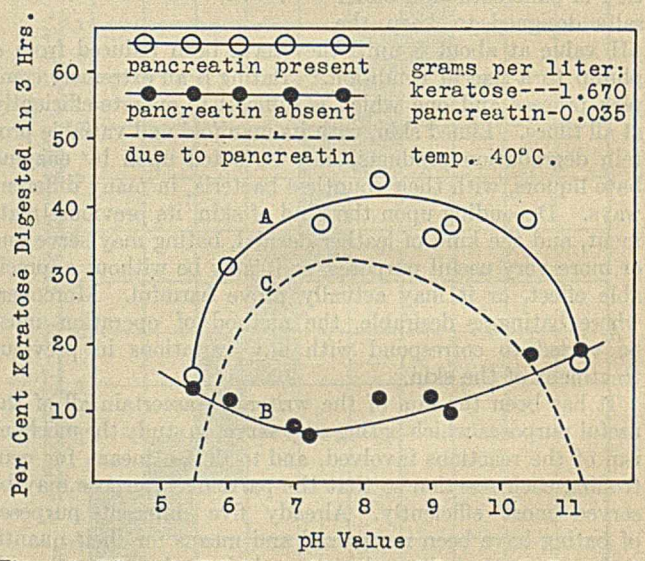


Figure 2—Effect of pH Value on Digestion of Keratose by Pancreatin

11.2, the enzyme is without effect, while it shows its optimum action at pH = 7.9. The range of comparatively great activity extends from about 7.5 to 8.3, which is the range ordinarily found in bate liquors.

Effect of Time

The progress of the digestion of keratose by pancreatin with time is illustrated in Figure 3. For comparison, a blank and a solution of a typical commercial bate are included. The curves are typical of protein hydrolysis by

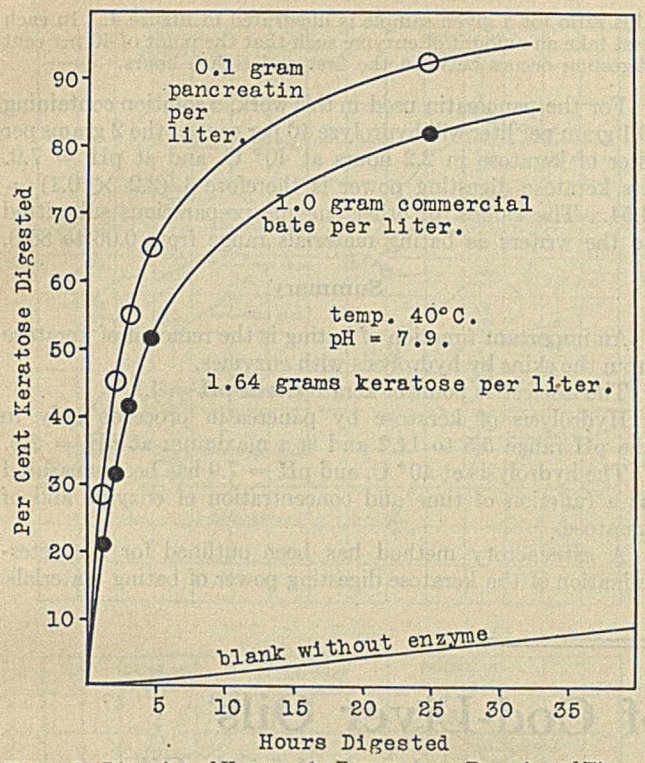


Figure 3—Digestion of Keratose by Enzymes as a Function of Time

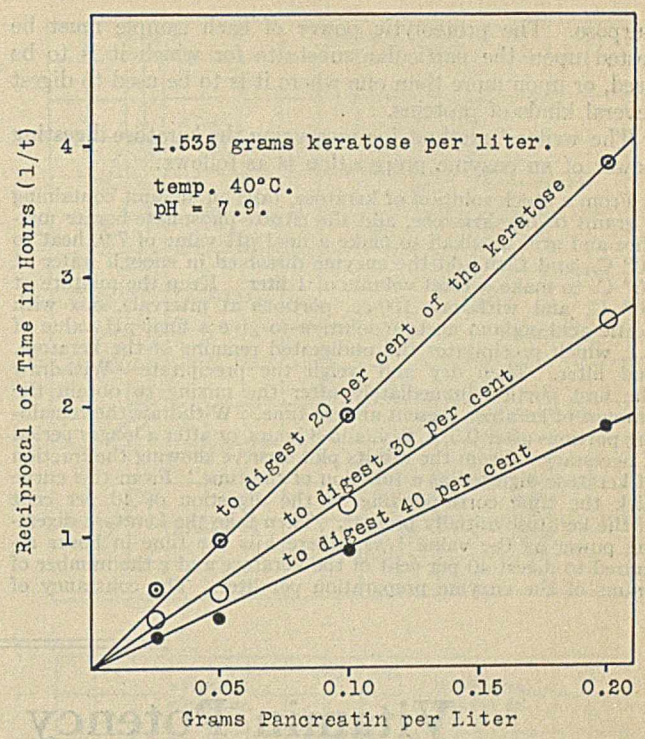


Figure 4—Rate of Digestion of Keratose as a Function of Concentration of Pancreatin

enzymes and the curve for the blank shows that during the first 24 hours practically all the digestion is due to the enzyme.

Effect of Concentration of Enzyme

With enzyme content the only variable, it was found that the time required to hydrolyze a given fraction of the keratose is inversely proportional to the concentration of enzyme. This is shown strikingly by the straight lines in Figure 4, where the reciprocal of the number of hours required to digest 20, 30, and 40 per cent of the keratose, respectively, is plotted against the initial concentration of the enzyme.

Effect of Concentration of Keratose

For a given initial concentration of enzyme, the rate of digestion increases with the value for the initial concentration of keratose. This is indicated in Figure 5, where the time required to hydrolyze a given fraction of the keratose present is plotted against the initial concentration of keratose. Where 2 grams per liter of keratose are present 0.8 gram is hydrolyzed in 135 minutes, but where 4 grams per liter are present 0.8 gram is hydrolyzed in only 93 minutes.

Comparison of Proteolytic Powers of Different Enzyme Preparations

Attempts have been made to determine the bating power of enzyme preparations by measuring their power to hydrolyze gelatin or casein, but it has been found that one cannot judge the proteolytic power of an enzyme preparation as regards one kind of protein from its action upon another protein. For example, on experimenting with two enzyme preparations both of which hydrolyze keratose, it is found that one of them is apparently without effect upon elastin, while the other hydrolyzes it readily. Commercial enzyme preparations are usually mixtures of several enzymes, which may be present in very different proportions in different preparations. Thus the sample showing the higher proteolytic power for one protein may show a lower power for another protein. One tanner may bate his stock to remove elastin, another to digest some of the collagen, and another the keratose. If given a dozen different enzyme samples to select from, it is probable that each would find a different one to be the most active bating material for his

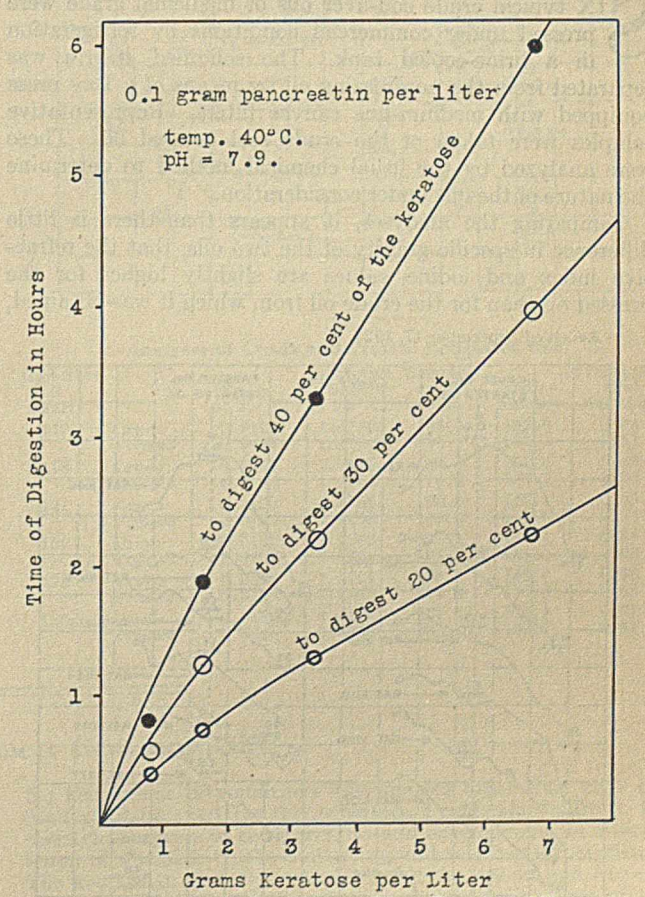


Figure 5—Time Required to Digest a Given Fraction of Keratose as a Function of Initial Concentration of Keratose

purpose. The proteolytic power of each sample must be tested upon the particular substrate for which it is to be used, or upon more than one where it is to be used to digest several kinds of proteins.

The writers' method for measuring the keratose digesting power of an enzyme preparation is as follows:

From a stock solution of keratose, take an amount containing 2 grams of dry keratose, add the citrate-phosphate-borate mixture and acid or alkali to make a final pH value of 7.9, heat to 40° C., and then add the enzyme dissolved in enough water at 40° C. to make a total volume of 1 liter. Keep the mixture at 40° C. and withdraw 100-cc. portions at intervals, mix with acetic acid–sodium acetate solution to give a final pH value of 4.1, which precipitates the undigested remains of the keratose, and filter. Then dry and weigh the precipitate. Withdraw the first portion immediately after the mixing to obtain the amount of keratose present at zero time. Withdraw the remaining portions after 0.5, 1, 2, 4, and 8 hours, or after a longer period if necessary. From the results plot a curve showing the fraction of keratose digested as a function of the time. From this curve pick the time corresponding to the digestion of 40 per cent of the keratose initially present. Then take the keratose digesting power as the value $1/hg$, where h is the time in hours required to digest 40 per cent of the keratose and g the number of grams of the enzyme preparation per liter. The constancy of this ratio for a given sample is illustrated in Figure 4. In each test take an amount of enzyme such that the point of 40 per cent digestion occurs between the first and eighth hours.

For the pancreatin used in this work, a solution containing 0.1 gram per liter will hydrolyze 40 per cent of the 2 grams per liter of keratose in 2.2 hours at 40° C. and at pH = 7.9. Its keratose digesting power is therefore $1/(2.2 \times 0.1) = 4.54$. The values for other enzyme preparations submitted to the writers as bating materials range from 0.06 to 86.0.

Summary

An important function of bating is the removal of keratose from the skins by hydrolysis with enzymes.

The isoelectric point of keratose is at pH = 4.1.

Hydrolysis of keratose by pancreatin proceeds only in the pH range 5.5 to 11.2 and is a maximum at pH = 7.9.

The hydrolysis at 40° C. and pH = 7.9 has been measured as a function of time and concentration of enzyme and of keratose.

A satisfactory method has been outlined for the determination of the keratose digesting power of bating materials.

Vitamin Potency of Cod-Liver Oils[1]

XVIII—Effect on Vitamin Potency of Cold-Pressing Cod-Liver Oils

By Arthur D. Holmes and Madeleine G. Pigott

The E. L. Patch Co., Boston, Mass.

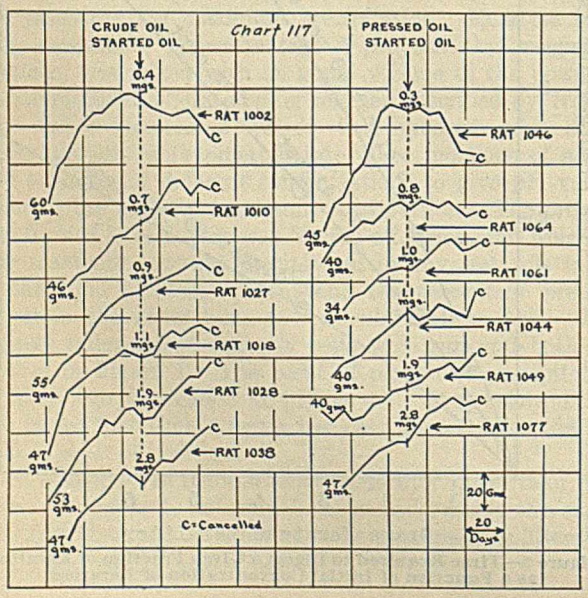
SIX typical crude cod-liver oils of medicinal grade were pressed under commercial conditions by refrigeration in a brine-cooled tank. The solidified stearin was separated from the nonfreezing oil by means of a Bay press equipped with medium-fine canvas filters. Representative samples were taken of the crude and pressed oil. These were analyzed by the usual chemical method to determine the nature of the oils under consideration.

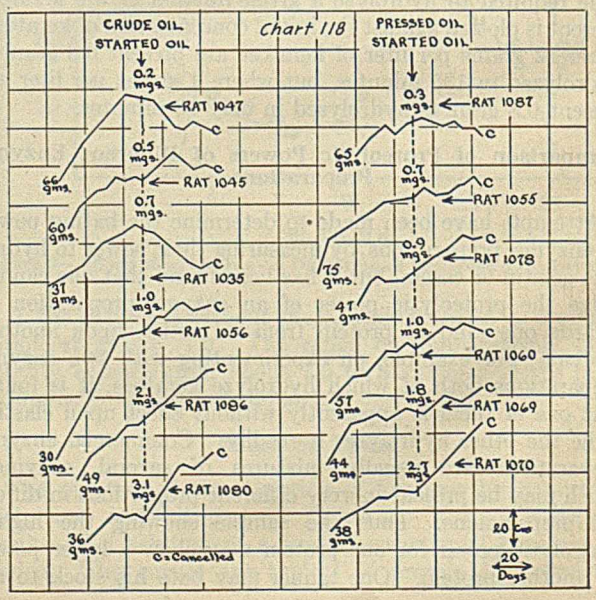
Comparing the analyses, it appears that there is little difference in specific gravity of the two oils, that the refractive index and iodine values are slightly higher for the pressed oil than for the crude oil from which it was obtained, and that the saponification and acid values vary for different oils. Considering the analyses as a whole, there appears to be little difference between the chemical and physical characteristics of crude and pressed cod-liver oils of the type under consideration.

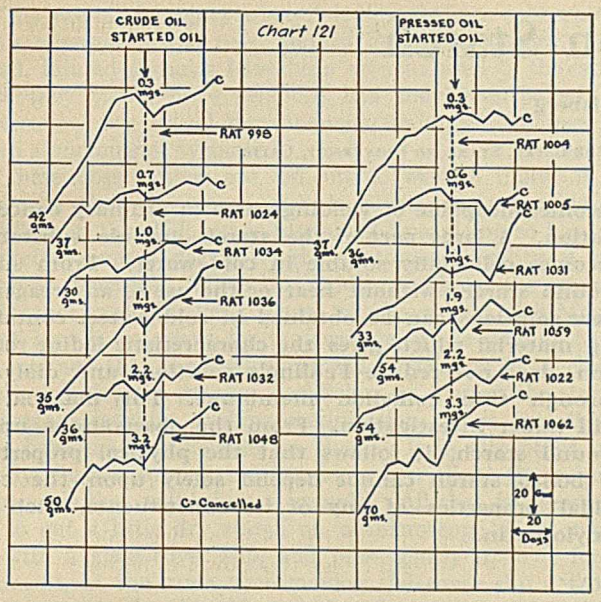
The vitamin potency of the oil under consideration was determined by the usual laboratory procedure which has already been described in detail.[2] Six experimental animals whose body reserve of vitamin A had been exhausted were assigned to each of the oils to be tested. The oil was fed separate from the experimental diet in amounts varying from

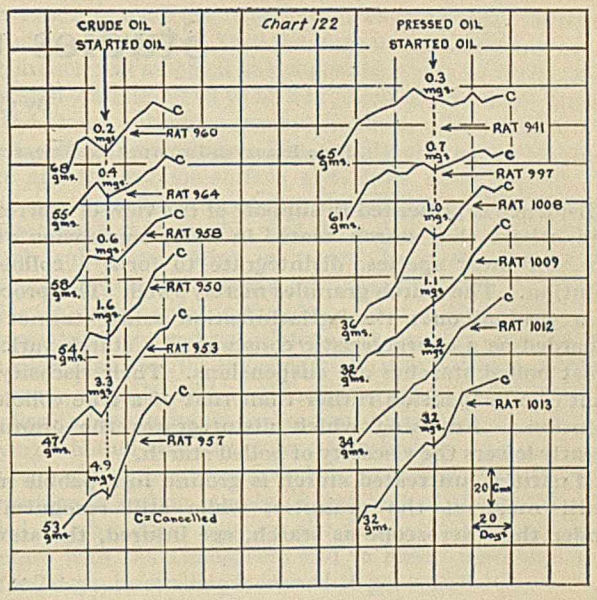
[1] Received September 17, 1925.

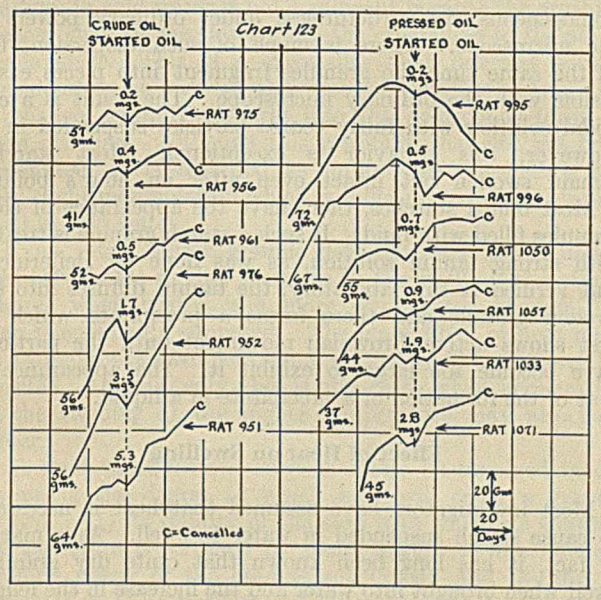
[2] *J. Metabolic Research*, **2**, No. 3 (September, 1922); This Journal, **16**, 1181 (1924); **17**, 75 (1925).

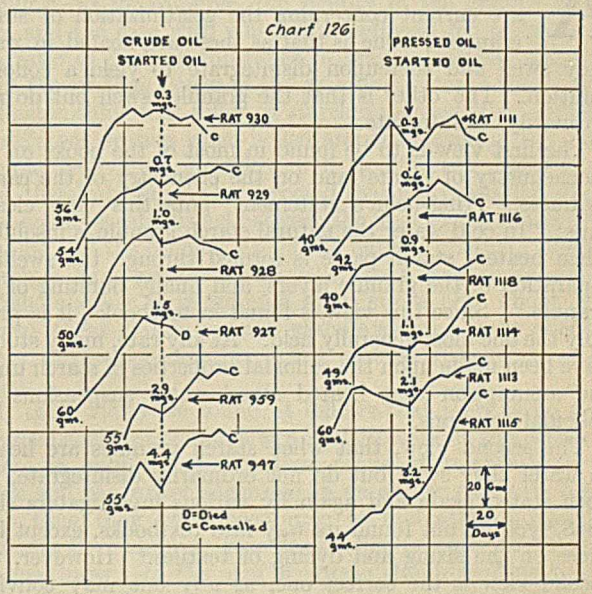












about 0.2 or 0.3 mg. to about 5 mg. daily. For the sake of convenience, the usual curves showing the food intake of the experimental animals have been omitted, and the growth curves for both the crude and pressed oils have been combined in the same chart.

As will be noted from the accompanying charts, the vitamin potencies of the crude and pressed oil from the same lot were not identical. Considered from a practical standpoint, however, the results of the biological tests reported above do not indicate significant difference between the potency of the crude and pressed oils.

Analyses of Crude and Pressed Cod-Liver Oils

Cod-liver oil chart		Sp. gr. at 20° C.	Refractive index at 25° C.	Saponification value	Iodine number	Free fatty acid Per cent
117	Crude	0.9192	1.4759	195.3	152.6	0.52
	Pressed	0.9198	1.4765	196.9	158.5	0.57
118	Crude	0.9198	1.4747	198.8	151.6	0.59
	Pressed	0.9198	1.4762	196.8	156.2	0.56
121	Crude	0.9192	1.4758	190.0	146.1	0.50
	Pressed	0.9195	1.4768	189.0	151.6	0.55
122	Crude	0.9195	1.4762	195.1	145.4	0.54
	Pressed	0.9199	1.4768	194.8	151.0	0.62
123	Crude	0.9189	1.4761	194.1	148.6	0.49
	Pressed	0.9189	1.4769	195.8	155.0	0.53
126	Crude	0.9199	1.4751	171.6	140.7	0.37
	Pressed	0.9205	1.4764	189.1	153.7	0.67

Universal Oil Products Company Gift

The Universal Oil Products Company, in announcing its pledge of $250,000 available beginning 1926, at an annual rate of $50,000, and duplicating that of John D. Rockefeller, states that it has had plans for establishing scholarships in universities and colleges for the study and development of the pure science of petroleum. It now finds that the results can be more quickly attained by concentrating such work under one directing body. No restrictions or conditions are imposed other than that the fund shall be used by the American Petroleum Institute for scientific purposes in the search for and development, in a broad sense, of scientific truths underlying and relating to petroleum. The knowledge thus derived will be for the benefit and free use of the industry, thus indirectly advancing the interests of the general public.

Studies upon Starch[1]

By Carl L. Alsberg

Food Research Institute and Department of Chemistry, Stanford University, Calif.

Evidence is presented in support of the view of Harrison and others that starch heated in water suspension does not, for most species, disintegrate to form a colloidal solution. The starch granules merely swell. The process is a gradual one; the "gelatinization point" cannot be regarded as a characteristic constant of a starch variety. Most boiled starches are suspensions. Their viscosity is that of a suspension rather than that of a true colloidal solution. Anything which disintegrates the granules greatly lowers the viscosity of boiled starch.

If natural, untreated starch is ground in a pebble mill until most of the granules, while still recognizable under the microscope as starch, are injured, the starch becomes incapable of yielding paste in ordinary concentration. A large part of the starch granule substance becomes colloidally soluble in cold water. From such ground starch, without heat or the use of any reagent, clear solutions can be obtained in cold water, containing material which gives the characteristic iodine reaction, does not reduce Fehling's solution, and dialyzes through thin collodion membrane. This material is still under investigation. From the observations upon ground starch, it follows that the physical properties of boiled starch cannot depend solely upon the colloidal properties of any of its constituents, such as amylopectin.

As one reads the literature one finds that two views are current concerning the gelatinization of starch granules. One is that as these are heated in water they swell and thereupon disintegrate to yield a colloidal solution. The other is that the granules swell but do not, ordinarily, disintegrate.

The first view is to be found in most of the books on the biochemistry of plants[2] and on the chemistry of the carbohydrates. Pringsheim's statement[3] puts this view clearly thus: "In cold water the natural starch granule is insoluble; when heated, starch paste is formed through the swelling, separation of the granule layers, and finally bursting of the granule." Since this view is found in textbooks, it is probably the one most generally held. At any rate, many studies have been made upon the colloidal properties of starch under the assumption that heated starch-water suspensions are colloidal solutions.

The second view, that when starch granules are heated in water they swell but do not ordinarily disintegrate, has been stated again and again by various investigators since 1848,[4] yet has not found its way into textbooks, except into those on the sizing and dyeing of textiles.[5] However, this second view is the correct one, as any one may convince himself by using the microscope.

Possibly the failure of this theory to gain general recognition is due to the fact that in Europe the most common commercial starch is that of the potato, in consequence of which this starch has been studied probably more than all others put together. Potato starch presents rather an exceptional behavior. Although the majority of starches examined at Stanford swell when heated in water, but do not burst, even after continued boiling, the starch of the potato gradually fragments and disintegrates, as pointed out by Harrison.[4] The process as observed under the microscope in this laboratory is not a uniform dispersion of the starch substance to form a colloidal solution that appears homogeneous and structureless under ordinary powers of the microscope. There is much of such dispersion, but at the same time the granules fragment into pieces easily visible with the ordinary microscope. The result is a colloidal solution with fairly coarse particles suspended in it. However, this behavior is exceptional. Most starches remain swollen but intact even after an hour's boiling.

Most boiled starches, then, have the appearance of clear granules filled with fluid. If such a starch granule is treated with strong tannin solution, as was done by Beijerinck,[4] and verified in this laboratory, the tannin diffuses into the swollen granule and there forms a precipitate which at first shows active Brownian movement until the particles have become too large to exhibit it. The appearance is that of the formation of a precipitate in a liquid.

Effect of Heat on Swelling

Most investigators have assumed that heat is necessary to cause starch suspended in water to swell. As a matter of fact, it has long been known that quite dry granules swell when brought into water and the increase in the length of their axes may be as great as 15 per cent or more.[6] When the granule has swelled, it has been assumed that further swelling does not take place unless the granule is heated. Hence, Meyer believed the two kinds of swelling to be quite different phenomena. The first he called "pore swelling," since it was supposed to be the result of the filling of the pores of the granule. The second he called "solution swelling," because it was assumed to be the result of the conversion of the solid crystalline starch substance into an emulsion colloid. This view has not been accepted generally,[7] and does not seem to be sound.

The basic assumption underlying the idea that the swelling of a dry granule in cold water is a different phenomenon from its swelling in warm water is quite unwarranted. This assumption is that the granule substance is incapable of swelling much in cold water. As a matter of fact this is not so. It has long been known[8] that a natural starch granule that has been injured mechanically so that it has been cracked, crushed, or merely has had a rift made into it, will swell

[1] Presented as a part of the Symposium on Chemistry and Plant Life before the joint session of the Divisions of Agricultural and Food Chemistry and Biological Chemistry at the 70th Meeting of the American Chemical Society, Los Angeles, Calif., August 3 to 8, 1925.

[2] For example, Czapek, "Biochemie der Pflanzen," 2nd ed., **1913**, Vol. I, p. 404. Jena.

[3] "Die Polysaccharide," 2nd ed., **1923**, p. 118. Berlin.

[4] Schleiden, "Principles of Scientific Botany," tr. by Lankester, **1849**, p. 13, London. Harrison, *J. Soc. Dyers Colourists*, **27**, 84 (1911); Beijerinck, *Koninklijke Akad. Wetenschappen Amsterdam, Proceedings of the Section of Sciences*, **14**, 1107 (1912).

[5] Cf. Nivling, "Starches, Their Fluidity and Viscosity in Relation to Sizing Value for Textiles." Barr-Erhardt Press, New York, **1924**.

[6] Meyer, "Die Stärkekörner," **1895**, p. 127. Jena.

[7] Cf. Samec, *Kolloidchem. Beihefte*, **3**, 123 (1912); Rothert, *Ber. botan. Ges.*, **15**, 239 (1897).

[8] Huss, *Arkiv Botanik*, **18**, Heft 2–3, 2 (1922–23).

at the site of the injury when it is brought into cold water. This observation has been verified in this laboratory. Indeed, injured granules have been seen to swell to the same size they would have achieved had they been boiled, as determined by actual measurement under the microscope with a micrometer eyepiece.[9]

These observations are difficult to explain unless it is assumed that the starch granule substance is capable of swelling in the cold, but is restrained from doing so beyond a certain limited degree by the anatomical rigidity of the granule structure. When this rigidity is relaxed the granule substance swells further. Those who have held with Meyer that heat is necessary for the swelling of the granule have maintained that the heat generated by friction in mechanically injuring the granule is sufficient to convert the starch substance into its swelling modification. This hypothesis has been made untenable by Huss.[8] It is altogether unlikely, furthermore, if one considers how slight the manipulation is that will injure a granule. All that is necessary is to put a little dry starch on a microscope slide, cover it with a glass cover slip, and press gently upon it for a moment, at the same time moving the cover slip a trifle.

It may further be objected that the swelling of cracked granules in cold water is not significant because the crushing process changes the starch from the crystalline to the amorphous state. This is a possibility that deserves serious consideration in view of the work of Ray,[10] who was able to change crystalline quartz into the amorphous form by mere grinding. Although this possibility has not yet been eliminated, it is regarded as improbable considering the very slight manipulation which is sufficient to make a granule swell in cold water.

If an intact starch granule does not swell much in the cold because its rigidity restrains it, the swelling of a starch granule when heated is a more complicated phenomenon than is commonly supposed. The main effect of heat must be to make the granules' structure less rigid and more distensible. Undoubtedly this is the case, while acceleration of the swelling at the higher temperature may also be a factor.

At least three factors must therefore be involved in determining the degree to which heat will cause a granule to swell: (1) its rigidity or the ease with which its anatomical structure is softened by moist heat; (2) the inherent swelling power of the granule substance; and (3) the relation of mass of swelling substance to surface area of the granule. The importance of the first two factors is obvious. The significance of the third is equally obvious if one considers that the volume of a sphere or its mass increases as the diameter is increased, much faster than its surface area. Therefore, the larger the granule the greater the mass of the swelling substance which exerts pressure upon the unit of granule surface. Given structure of identical rigidity in two granules of different diameter, it follows that the larger should swell more readily than the smaller one. It should swell sooner as the temperature is raised, because it will begin to exert enough intragranular pressure to distend the restraining structures of the granule before these have been softened to as great a degree as they must be to permit smaller granules to swell. Indeed, Nyman[11] has reported that in the same sample the smaller granules swell sufficiently to lose their bi-refringence at a higher temperature than the larger ones. This he attributes to greater thickness of the membrane enveloping the smaller granules as compared with that surrounding the larger ones. Whether or not this is the case, it is plain that small granules must swell less easily than large ones if both have the same initial rigidity.

Harrison has assumed the degree to which different kinds of starch granules swell to be a function of the colloidal state of the starch substance present in them. This assumption is altogether unnecessary. The rigidity of the granule structure and the volume–surface area ratio alone present variables enough to account for the difference in behavior. Nevertheless, it is possible that the colloidal condition of the starch substance varies in regard to swelling capacity, though it is believed this is a minor factor. Indeed, there is evidence on this point in the observation of Nyman that the temperature required to gelatinize thoroughly dried starch is higher than that for the same starch before drying. Measurements in this laboratory of the size of potato-starch granules swollen to the maximum by heating in water before and after drying, showed that the potato starch dried to a moisture content of 8 per cent reaches a size such that the area of its largest cross section is only 57 per cent of that of the undried starch. After allowing the dried starch to remain in contact with the atmosphere and to absorb moisture from it for 2 days, its swelling increased 10 per cent.[9]

Considering the many factors that are involved in the swelling—as for example, the rigidity of the granule structure and the ease with which it is softened by moist heat, the ratio of swelling substance to granule surface, and perhaps the swelling power of the granule substance itself—it is not astonishing that different starches increase their volumes to different degrees when boiled and that, even in the same sample, individual granules swell to different degrees. It was, therefore, only to be expected that no correlation whatever could be established between the final size of the swollen granule and the original size of the natural granule. Potato starch, a large granule sort, swells about forty times; canna starch, another large granule kind, swells only about 16.5 times; wheat starch, a small granule starch, swells about 8 times; arrowroot, another small granule starch, about 45 times.

If these views are sound, it follows that there is no such physical constant of starch as a "gelatinization" temperature. There is only a gelatinization range of temperature, as Rask and the writer suggested in an earlier paper.[12] Since that time they have been able to find other supporting evidence by measuring granules swollen in water at different temperatures. In the case of potato starch swelling begins below 50°. The size of the granule increases as the temperature is increased and does not reach its maximum till just below boiling. The process of swelling is a gradual one proceeding over a range of at least 50° C.

It may be concluded, then, that boiled starches are suspensions, not true colloidal solutions at all, unless they have been severally boiled or otherwise treated to disintegrate the suspended particles. Within the suspended swollen granules there is a colloid, probably colloidally dissolved. This conclusion is not new, though it is not generally current. This view, hitherto held only by a few textile chemists, has been elaborated, modified in important particles, and supported with new experimental evidence.

Character of Starch Paste

Just as there are two theories concerning the character of the swelling of starch granules, so there must be two views concerning the character of starch paste and the cause of its physical properties. Those who hold that starch granules swollen by heating in water disintegrate to form a colloidal solution believe that the viscosity of such a solution is due to the colloidally dissolved substance, just as the viscosity of

[9] Unpublished observations of Elizabeth P. Griffing.

[10] *Proc. Roy. Soc.* (*London*), **A101**, 509 (1922); **102**, 640 (1923); cf. also Beilby, "Aggregation and Flow of Solids," **1921**, p. 116. Macmillan.

[11] *Z. Nahr. Genussm.*, **24**, 671 (1912).

[12] Alsberg and Rask, *Cereal Chemistry*, **1**, 107 (1924).

a warm gelatin solution is due to the gelatin dispersed in it. They believe, further, that the setting of the system is nothing but ordinary gel formation.

If the view of the process of swelling of starch granules described above is correct, the above conception of the nature of the heated starch-water system and the causes of its viscosity and of its setting to a paste are impossible. The system is a suspension. Its viscosity must be akin to that of a suspension rather than that of a colloidal solution like a gelatin solution, and the setting to a paste cannot be a phenomenon entirely like the setting of an ordinary gel.

Harrison has shown that anything that breaks up the swollen granules—as, for example, vigorous shaking—greatly reduces the viscosity of boiled starches and the stiffness of the paste to which they set. It has been shown in this laboratory that grinding very stiff starch paste in a pebble mill converts it into a sirup. Under the microscope the swollen granules are seen to be disintegrated. Still more interesting are experiments upon grinding ordinary starches dry in a pebble mill.[13] If starch is ground until under the microscope most of the granules appear chipped or cracked or frayed, but still recognizable as starch, it is incapable of producing paste in any ordinary concentration. In the case of potato starch a concentration in the neighborhood of 10 per cent is necessary to get a paste, the exact concentration depending upon the intensity of grinding. Examination under the microscope shows that granules in large numbers are disintegrated.

It has already been stated that injured granules swell in cold water. Examination of dry ground starch shows that they not merely swell, but also disperse to a large extent in cold water. Over 60 per cent of some samples of ground starch passed readily into colloidal solution in cold water. The granules had not been reduced to an impalpably fine submicroscopic dust. Any one would recognize most of them with the microscope as starch grains, though perhaps battered. Opalescent solutions have been obtained without any heating whatever with almost 10 per cent of starch in them. Their viscosity was that of a thick sirup and increased somewhat on standing. This seems to answer the question on which there has been no agreement among investigators hitherto—whether or not the natural starch granule contains any substance which is soluble in water without heating. Moreover, by a special method of filtration, without the use of heat at any stage or of any reagent, perfectly clear solutions almost optically void have been obtained, that contain 0.4 per cent of a substance giving an intense blue with iodine. This substance does not reduce Fehling's solution until after inversion and it dialyzes through thin collodion membranes.[14] It has been made the starting point of a series of investigations which will be reported later.

The reason why ground starch, in ordinary concentration, does not give paste is now clear. Boiled starch forms paste only when the ratio of starch to water is so chosen that the swollen granules occupy most of the volume of the system and therefore touch or jostle one another (Harrison, Beijerinck). The viscosity of a still warm, swollen starch suspension is for the greatest part the resultant of this jostling. When the granules are injured by dry grinding, rubbing the paste with sand (Beijerinck), or grinding in a pebble mill, a great part of the starch substance is dispersed in the solution; the undispersed portion occupies only a small part of the volume of the system, the viscosity of the system is not great and on cooling no paste forms.

As we have seen, the swelling of starch granules is dependent upon the softening of their naturally rigid structure by moist heat. The microscope shows that warm boiled starch granules are easily deformable and elastic. They can easily be made to move past one another, to flow. In paste they are much less easily deformable, much less elastic. At lower temperatures apparently a portion of the rigidity of the original starch is recovered. Possibly, too, the granule surfaces are more sticky, favoring their agglutination, one with the other. For these reasons it is more difficult to make the granules move past one another. The system can no longer be made to flow. Evidence that there is the setting of a gel within the granules has not been obtained. The fact that grinding paste releases the granule contents as a colloidal solution indicates, though it does not prove, that the granule contents is a colloidal solution in the cold. That very concentrated ground starch suspension may form paste is due to the fact that the colloidally dispersed starch substance is viscous in high concentrations and that the ground starch still contains more or less coarse suspended matter which swells when heated. Both factors are concerned in the setting to a paste of concentrated dispersions of ground starch. What is the relative importance, quantitatively, of the two, it is impossible to say. In this connection, it is interesting to note that a 10 per cent suspension of ground potato starch in cold distilled water is at first quite viscous and sirupy. On standing overnight it becomes much thicker and forms a gel that is mechanically very fragile.[9] Whether the change in consistency is due to a change of state of the dispersed starch substance, or to swelling of such granules or pieces of granules as are not wholly dispersed, is not known. At any rate, it seems quite certain that the consistency of boiled starches depends in very large measure upon the physical properties of the swollen granules. To the extent that the consistency depends upon such mechanical factors, it is not a colloid-chemical property at all.

If this be so, the hypothesis of Maquenne[15] concerning the cause of the viscosity of starch paste is untenable. He found—and it has been confirmed in this laboratory—that amylose, the major constituent of starch is incapable by itself of forming paste. He therefore assumed that amylopectin, which is localized chiefly in the starch envelope, swells and becomes gelatinous when starch is heated, and on cooling makes paste. He attributed the paste-forming power of starch to the colloid properties of amylopectin. Ling and Nanji[16] have accepted his views and support it by showing that treatment with dilute hydrochloric acid removes phosphoric acid and robs starch of its paste-forming properties. Since amylopectin is supposed to be a phosphoric acid ester which is saponified by hydrochloric acid, they assume that the action of hydrochloric acid is due to its amylopectin-destroying power. If such acid starch be watched as it is heated, one sees that it disintegrates. It does not swell and remain whole like natural starch. It may well be true that the paste-forming power of starch is dependent upon amylopectin, but this must be because amylopectin preserves the suspensoid character of boiled starches, since all agree it is localized chiefly in the outer layer of the granule. Its removal or depolymerization would then merely signify that the ability of the granule to remain intact, though swollen by heat, has been lost. Amylopectin has been prepared in this laboratory by the freezing method of Gatin-Gruzewska as modified by Ling and Nanji, but it has not been possible to prepare a paste from it.

The criticism might be made that grinding has changed its character from the crystalline to the colloid state. The question is being further investigated on starch and other substances, because it has been found that dry grinding does change the character of certain colloids. If dry gelatin is ground as the starch herein described was ground, it becomes

[13] Alsberg and Perry, *Proc. Soc. Exptl. Biol. Med.*, **22**, 60 (1924).

[14] Unpublished work of J. Field, 2nd.

[15] *Bull. soc. chim.*, [3] **35**, 769 (1906).

[16] *J. Chem. Soc. (London)*, **T123**, 2667 (1923).

much more soluble in cold water, yielding opalescent solutions from which a clear filtrate may be obtained that is not very viscous but contains enough gelatin to set to a gel on standing. The fineness to which the gelatin was ground does not even approach that attained by a colloid mill. The results of the investigation of this phenomenon now in progress may possibly require some modification in matters of detail of the views expressed in this paper. The main conclusion, however, that heated starch granules do not ordinarily disintegrate, and that the viscosity of boiled starches is in large part a function of the anatomical structure of the swollen granules, cannot be affected thereby.

Report of Surgeon General's Committee on Tetraethyl Lead

January 17, 1926

SURGEON GENERAL H. S. CUMMING
UNITED STATES PUBLIC HEALTH SERVICE
WASHINGTON, D. C.

Dear Sir:

The committee appointed by you at the request of the conference held in Washington, May 20, 1925, was directed to present to you "if possible by January first next, a statement as to the health hazards involved in the retail distribution and general use of tetraethyl lead gasoline motor fuel." As soon as practicable after its appointment, the committee met in your office for organization and for discussion of the procedure to be followed in carrying out its instructions.

The members of the committee familiarized themselves, as far as possible, by conferences and by reading, with the existing data bearing upon the subject and upon lead poisoning in general. They had access to the stenographic report [See *Public Health Bulletin* 158] of the addresses and discussions which took place at the conference of May 20, and subsequently they made a personal examination of the plant at Deep Water, N. J., for the manufacture of tetraethyl lead, and of one of the stations at which the ethyl fluid is mixed with gasoline.

Ethyl gasoline was first placed on sale February 1, 1923, and its sale was voluntarily discontinued May 5, 1925, about 300,000,000 gallons of ethyl gasoline being distributed during this period. Serious cases of poisoning occurred among men handling lead tetraethyl and ethyl fluid in the States of New Jersey and Ohio. As far as the committee is aware these accidents had all occurred in connection with the manufacture and blending of concentrated tetraethyl lead, and threw no direct light upon the problem specifically laid before us—that of the retail distribution and general use of ethyl gasoline. The valuable experiments reported by the U. S. Bureau of Mines and by investigators at Columbia University and others yielded important results, but we felt that the crucial test of the situation must be derived from actual experience in the use of ethyl gasoline under practical conditions of operation.

It was therefore decided that the committee should make a direct investigation of the question submitted to them, planning the work on as extensive a scale as was possible in the time allowed. Fortunately this mode of approach was made feasible by the fact that ethyl gasoline has been in constant use as a motor fuel in certain parts of Ohio for several years; and although the production and distribution of tetraethyl lead and ethyl fluid had been suspended by the voluntary action of the manufacturers, pending the present investigation, it was known that in the region indicated, a supply of ethyl fluid was still in the hands of certain consumers and would be continued in use. We were thus presented with an opportunity of studying a fairly large group of individuals who had been using and handling ethyl gasoline and of comparing the findings upon them with the examination of a similar group employing gasoline free from lead.

In several conferences, the committee, with the assistance of Surgeon General Cumming and Surgeon L. R. Thompson, U. S. Public Health Service, in charge of the section of Industrial Hygiene and Sanitation, formulated a general plan of investigation. The actual conduct of the work was entrusted to Dr. J. P. Leake, Surgeon, U. S. Public Health Service, who at once organized a corps of workers and began observations upon certain groups of individuals in Dayton and Cincinnati. The committee desires to express its appreciation of the cordial coöperation extended to this group of observers by both the employers and workers in the garages selected for the investigations. After all the preliminary arrangements had been completed, the work was pushed with great vigor during the autumn months, and on December 19, Dr. Leake presented to the committee a full report of the results of his study. The committee wishes to express its great satisfaction with the promptness, energy and ability with which these investigations were carried out. The general character and scope of the work may be summarized briefly as follows:

Two hundred and fifty-two individuals were studied. They were all adult males, and fall into five groups.

1—Group A, a control group, consisted of thirty-six men who were employees of the City of Dayton. Their duty was to drive cars during the working day. In these cars the gasoline used contained no lead. The cars were housed in the municipal garage, which in the report is designated as the Dayton Control Garage.

2—Group B, a test group, consisted of seventy-seven men who were employees of a public service corporation in Dayton, and whose duties were similar to those of Group A. The cars that they drove, however, used ethyl gasoline, and this fuel had been in constant use in this service since July, 1923. The garage in which these cars were housed is designated as the Dayton Test Garage.

3—Group C, a control group, consisted of twenty-one men. These were employed as garage workers in the Dayton Control Garage or in a similar control garage in Cincinnati, or as gasoline fillers at service stations or on trucks delivering gasoline in Dayton and the adjoining region. In none of these garages, service stations, or trucks was gasoline containing lead used or handled.

4—Group D, a test group, consisted of fifty-seven men. These were employed as garage workers in the Dayton Test Garage or in a similar test garage in Cincinnati, or as gasoline fillers at service stations, wholesale gasoline plants, or on trucks delivering gasoline in Dayton, Cincinnati, and vicinity. The duties of these men were similar to those of Group C except that ethyl gasoline was handled in the garages, stations, and trucks.

5—Group E, a control group, consisted of sixty-one men employed in two industrial plants of entirely different character from the foregoing in which there was known to be a serious exposure to lead dust. Numerous cases of lead poisoning had occurred in these plants. This group was selected to serve for what might be called a positive control or check in regard to the validity of the clinical and analytical methods used in the study of the individuals of Groups A, B, C, and D.

Methods Used

Each individual was subjected to a careful clinical examination, and in addition, smears were made from his blood and a specimen of his feces was collected. The blood smears and the fecal specimens were sent to Washington to be examined by trained experts for stippling of the red cells and for content in lead. The examination of the feces for lead was made by chemists who had been especially trained in the technic of the method.

The blood examinations were made by a group of skilled observers, and were arranged so that the counts in each case were checked by several workers.

The clinical examination was conducted by four physicians. The first of these took a careful industrial history of each subject, and assigned to him a certain number. These numbers were taken at random. Thereafter this individual was recorded by his number, and none of those making the subsequent examinations or the laboratory tests knew whether or not the individual had been exposed to ethyl gasoline; nor, in fact, did any examiner, except the one who took the industrial history, know to which group the individual belonged.

After taking the industrial history, other examiners made a thorough medical examination, including a medical history, hemoglobin estimation, red-cell count, blood pressure records, visual acuity tests, urine examinations, etc.; and finally a determination, by a special method devised for the occasion, of the muscular strength of the extensor and flexor muscles of the forearm.

While all of the examinations were made with as much care as possible, special attention was given to three methods which, it was hoped, would yield quantitative data of an objective character. These were, first, the determination of the amount of lead in the feces, as an index of lead ingestion or absorption; second, the estimation of the number of stippled red cells, which, in the absence of other causes, might also be considered as an index of lead absorption; third, measurements of the strength of the extensor muscle of the forearm, as an index of lead poisoning. The first two methods yielded results of positive value, but the last was practically negative so far as the present investigation is concerned.

Results

When all the data had been collected, they were submitted to study and statistical analysis by Dr. Leake and his collaborators, and the results were presented to the committee in the form of a detailed report containing a description of the methods used, tabular summaries of results, and protocols of the findings for each individual studied. This report will be published in full by the Public Health Service. So far as the clinical examinations are concerned, it may be said that they failed to give any decisive indication of lead poisoning among the chauffeurs or workers in garages in which ethyl gasoline was used as a motor fuel (Groups B and D).

Note—The only injury observed was acute irritation of the eyes in a few cases, due to getting gasoline into the eyes. This occurred both with ordinary gasoline and with ethyl gasoline but was perhaps more severe in one case due to the latter. This case is mentioned specifically in the full report.

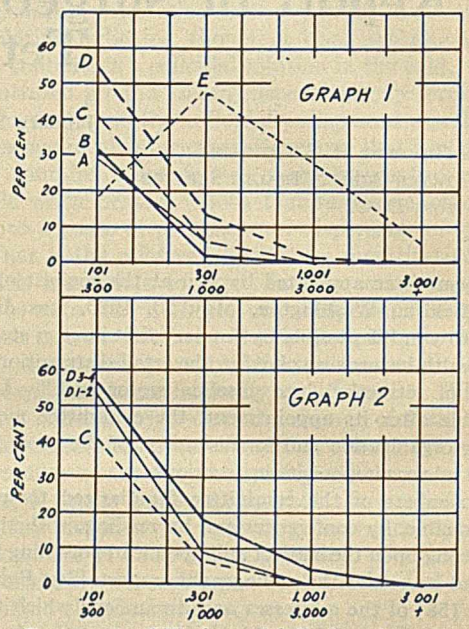
The median time of potential exposure among these men approximated two years, and this negative result, therefore, holds good only for a period of this duration. It should be added that in Group E, comprising workers in industrial plants in which there was a known and serious exposure to lead dust, definite clinical symptoms of lead poisoning were revealed, although these workers had been exposed for shorter periods of time.

Table A—Percentage of Persons with More than 0.1 Mg. of Lead per Gram of Ash in Feces

Group	Milligrams of Lead per Gram of Ash			
	0.101–0.300	0.301–1.000	1.001–3.000	3.001 and over
A	29	6	..	..
B	32	2	..	..
C	41	6	..	..
D	56	13	2	..
E	15	49	29	5

More significant results were obtained from the analysis of the feces and from the microscopic examination of the blood smears. These results are presented in condensed form in the accompanying graphs and tables. (Graphs 1 to 4 and Tables A, B, C, and D)

Graph 1 and Table A represent the amount of lead found in the feces of the individual of Groups A, B, C, D, and E. The figures along the abscissa of the graph give the amount of lead in milligrams per gram of ash of the feces, from 0.1 mg. to 3 mg. The ordinates represent percentages of the workers in each group. It will be seen that in Groups A and B, representing drivers of cars, one using gasoline without lead and the other ethyl gasoline, the amount of lead in the feces was practically identical. The exposure of these men was mainly to the exhaust gas from the



Percentage of Workers with Various Amounts (0.1 Mg.) of Lead per Gram of Ash in Feces by Groups

motors, and it would appear that in Group B, using the ethyl gasoline, there was no positive indication of increased absorption of lead. The fact that in Group A some lead was also found in the feces shows that these men were exposed to lead from some other undetermined source. In this connection it is to be noted that twenty examinations were made in Washington by the same methods of the feces of ten of the workers in the Hygienic Laboratory of the U. S. Public Health Service. These workers had had no known exposures to lead but their feces showed at each examination small amounts of lead ranging from 0.047 mg. to 0.290 mg. per gram of ash of the feces. In what might be called normal feces, therefore, lead may be present, from accidental exposures of one kind or another, in concentrations not differing materially from those found in Groups A and B.

Table B—Percentage of Persons with More than 0.1 Mg. of Lead per Gram of Ash in Feces

Group	Milligrams of Lead per Gram of Ash			
	0.101–0.300	0.301–1.000	1.001–3.000	3.001 and over
C	41	6	..	..
D1 and D2[a]	54	8	..	..
D3 and D4	57	18	4	..

[a] D1 and D2 are the two quarters of exposure Group D, which had less exposure to ethyl gasoline and ethyl fluid, and D3 and D4 are the two quarters which had the greater exposure.

In Group C, representing the garage workers and gasoline handlers not exposed to ethyl gasoline, there is an indication of a slightly greater excretion of lead. In the control garages and repair shops, as will be shown later, there was a perceptible amount of lead in the dust upon the floors and benches.

In Group D, representing the garage workers and gasoline handlers using ethyl gasoline, there is a still further increase in the amount of lead excreted, although the number who showed excretion of as much as 0.3 mg. per gram of ash is small (15 per cent). It seems probable that this increase was due to the use

of ethyl gasoline, since subdivision of this group into two classes, those with a lesser exposure to ethyl gasoline, as regards time and intensity, D1 and D2, and those with a greater exposure, D3 and D4, indicates that in the latter there was greater excretion, as is shown in Graph 2 and Table B.

In Group E, as would be expected, there is evidence of much greater ingestion or absorption: Over 80 per cent showed more than 0.3 mg. of lead for each gram of ash of the feces, and in some cases the lead was present in concentrations as great as 3 mg. per gram of ash.

Table C—Percentage of Persons Showing Definite Stippling of Different Degrees

Group	Stippled Cells per 100,000 Red Cells 1–2	3–6	7–20	21–100	Over 100
A	6	..	3	3	..
B	9	3	..	..	..
C	19	5	..	..	..
D	28	9	9	..	..
E	10	13	13	26	31

Graph 3 (see Table C) gives curves indicating the number of stippled cells found in the blood of the workers in Groups A, B, C, D, and E. The abscissa in this case represents the number of definitely stippled cells per 100,000; the curves are plotted for the values 1 to 2 per 100,000, 3 to 6, 7 to 20, 21 to 100.

Here again the results for Groups A and B are practically identical. In each group a small number, 12 per cent, showed definite stippling. No examinations of persons who are neither drivers of cars nor garage workers are available, carried out by the same observers using the same method. It is not possible to say whether the slight degree of stippling observed with Groups A and B possesses any significance, but it seems to be clear that the members of Group B, exposed to the exhaust gases from engines using ethyl gasoline, showed no noticeable increase in stippling as compared with Group A.

Table D—Percentage of Persons Showing Definite Stippling of Different Degrees

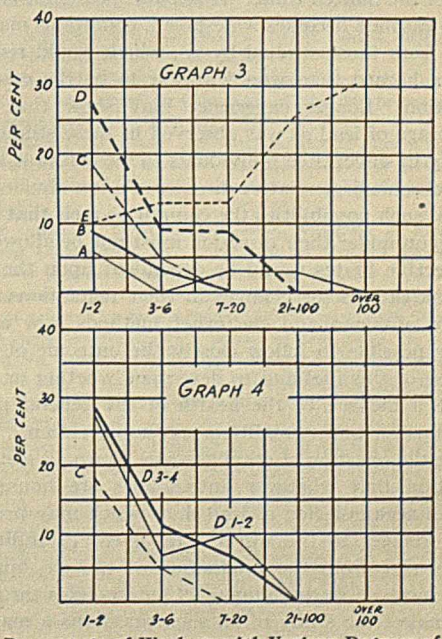
Group	Stippled Cells per 100,000 Red Cells 1–2	3–6	7–20	21–100	Over 100
C	19	5	..	..	..
D1 and D2[a]	28	8	10	..	..
D3 and D4	29	11	8	..	..

[a] D1 and D2 are the two quarters of exposure group D, which had less exposure to ethyl gasoline and ethyl fluid, and D3 and D4 are the two quarters which had the greater exposure.

In Group C there is a distinct increase in the percentage of workers showing stippling, and this increase is more marked in the workers of Group D. These results, therefore, corroborate the findings from the analysis of the feces in suggesting a beginning storage of lead in these two groups. That the greater indicated storage in Group D is connected with the use of ethyl gasoline seems to be borne out by the curves shown in Graph 4 (Table D), in which the curves are plotted for the two classes of Group D referred to above, the workers with the greater exposure showing a very slight increase in the percentage of those exhibiting definite stippling. The curve for the workers in Group E is of an entirely different character. Over 90 per cent showed distinct stippling, and in most of these cases the stippling was relatively very abundant.

Inquiry into Reported Cases of Injury Resulting from the Use of Ethyl Gasoline. So far as the committee could ascertain, all the reported cases of fatalities and serious injuries in connection with the use of tetraethyl lead have occurred either in the process of manufacture of this substance or in the procedures of blending and ethylizing. It seemed desirable to institute an inquiry in the region where this investigation was made, and where ethyl gasoline had been employed as a motor fuel for the longest time, as to possible cases of injury resulting from its use. All the workers examined were questioned, therefore, in regard to their knowledge of cases of possible injury, and inquiries were made in the Dayton and Cincinnati districts among local health officers, physicians, public health workers, and labor leaders. The few clues obtained from this inquiry were investigated in detail, but the results were negative. No positive evidence could be obtained of harmful effects attributable to the use of ethyl gasoline.

Observations upon the Lead in the Dust and Air of the Garages Investigated and upon the Amount of Carbon Monoxide. In addition to the examinations made upon the workers themselves, some data were collected in regard to the amount of lead in the air and dust of the garages and work rooms, and also in regard to the concentration of carbon monoxide. These observations were made during October, 1925, and owing to the unusually cool weather prevailing during that month the doors and windows were closed during most of the day. The conditions regarding ventilation were those to be expected for winter rather than summer weather. The several methods employed in this part of the investigation are given in detail in the full report. The findings obtained are summarized in the accompanying tabular statements for the several garages investigated as well as for the industrial plants in which there was a serious exposure to lead dusts. This part of the investigation was not so extensive as was desired, owing to the shortness of the time allowed, but it is evident from the results obtained that some lead was present in the air of the garages and work rooms whether the gasoline used contained lead or not; and in the sweepings of dust from the floors and benches there was a distinct amount of lead present, the figures running from 0.82 mg. to 22.31 mg. per gram of dust, according to the time and place of the gathering of the sample. It would seem probable, therefore, that in all garages in which automobiles are being handled and repaired, the workers are constantly exposed to certain amounts of lead dust, and this fact would tend to emphasize the importance of providing such rooms with adequate ventilation, and of keeping both the floors and the benches as free as possible from the accumulation of dust. Owing to the incompleteness of the data, it is not possible to say definitely whether the exposure to lead dust was greater in those garages in which ethyl gasoline was used. It is very desirable that these investigations should be continued.



Percentage of Workers with Various Degrees of Stippling (Definite) by Group

Conclusions

On the basis of this investigation, the committee feels that the following general conclusions are justified:

1—Drivers of cars using ethyl gasoline as a fuel and in which the concentration of tetraethyl lead was not greater than 1 part to 1300 parts by volume of gasoline, showed no definite signs of lead absorption after exposures approximating two years.

2—Employees of garages engaged in the handling and repairing of automobiles and employees of automobile service stations may show evidence of lead absorption and storage, as indicated by the lead content of the feces and the appearance of stippled cells in the blood. In garages and stations in which ethyl gasoline was used, the amount of apparent absorption and storage was somewhat increased, but the effect was slight in comparison with that shown by workers in other industries when there was a severe lead hazard (Group E) and for the periods of exposure studied was not sufficient to produce detectable symptoms of lead poisoning.

3—In the regions in which ethyl gasoline has been used to the greatest extent as a motor fuel for a period of between two and three years, no definite cases have been discovered of recognizable lead poisoning or other disease resulting from the use of ethyl gasoline.

In view of these conclusions your committee begs to report that in their opinion there are at present no good grounds for prohibiting the use of ethyl gasoline of the composition specified, as a motor fuel, provided that its distribution and use are controlled by proper regulations. The committee feels that the formulation of specific regulations in regard to the manufacture, distribution, and use of tetraethyl lead, ethyl fluid, and ethyl gasoline for adoption and enforcement by the several States belongs properly to the office of the Surgeon General of the Public Health Service. In an appendix to this report, attention is called to certain suggestions which have been made in the course of the discussions of this committee and which it is believed should be taken into consideration in making such regulations.

In conclusion, we beg to say that we are conscious of the fact that the conclusions to which we have come in this report, although based upon most careful conscientious investigations, are subject to the criticism that they have been derived from the study of a relatively small number of individuals who were exposed to the effects of ethyl gasoline for a period of time comparatively brief when we consider the possibilities in connection with lead poisoning. A more extensive study was not possible on account of the limited time. It remains possible that, if the use of leaded gasoline becomes widespread, conditions may arise very different from those studied by us, which would render its use more of a hazard than would appear to be the case from this investigation. Longer experience may show that even such slight storage of lead as was observed in these studies may lead eventually in susceptible individuals to recognizable lead poisoning or to chronic degenerative diseases of a less obvious character. In view of such possibilities the committee feels that the investigation begun under their direction must not be allowed to lapse. The respective States would be dependent upon the findings of such investigations for changes in their regulations. With the experience obtained and the exact methods now available, it should be possible to follow closely the outcome of a more extended use of this fuel and to determine whether or not it may constitute a menace to the health of the general public after prolonged use or under conditions not now foreseen.

Outside the question of ethyl gasoline, it would seem from this investigation that wherever automobiles are housed together there is an accumulation of lead dust which may prove to be a source of danger to the workers involved, in addition to the hazards arising from the production of carbon monoxide gas. The vast increase in the number of automobiles throughout the country makes the study of all such questions a matter of real importance from the standpoint of public health, and the committee urges strongly that suitable appropriation be requested from Congress for the continuance of these investigations under the supervision of the Surgeon General of the Public Health Service, and for a study of related problems connected with the use of motor fuels.

W. H. Howell, *Chairman*
A. J. Chesley
David L. Edsall
Reid Hunt
W. S. Leathers
Julius Stieglitz
C.-E. A. Winslow

Muscle Shoals Report

As has been announced in the daily press, the Muscle Shoals Commission appointed by the President has made a majority and a minority report. That such might be the case was apparent to all those conversant with the Muscle Shoals problem at the time the commission was appointed, for the views of those supporting the majority report were already well known. These are Messrs. McKenzie, Dial, and Bower. The extent to which the majority sought to impose its will upon the whole commission was evidenced when the chairman took it upon himself to organize the commission and appoint a technical advisor and a secretary before the commission had ever met. The report of the majority is really a political document evidently written with a view to what could be put through Congress. The facts presented by scientists and engineers have been disregarded, and while the report does favor the leasing of the facilities to private bidders if a suitable contract can be made, it continues to tie up the potentialities of Muscle Shoals with the "cheap" fertilizer question and favors government operation if a satisfactory private bid cannot be obtained.

Majority Report

Pertinent paragraphs from the majority report follow:

A majority of the members of the inquiry are fully persuaded that the plain mandate of section 124 of the national defense act of 1916, safeguarding the national defense and further providing for the use of the plants and power for the benefit of agriculture in time of peace, cannot be ignored. Muscle Shoals plant was built for the purpose of providing nitrogen compounds fixed from the air, to be used for explosives in time of war, and the manufacture of fertilizers in time of peace; not as a hydroelectric power-generating station for distribution purposes. The members of the inquiry, having this in mind, are convinced that nitrogen fixation plants No. 1 and No. 2, located, respectively, at Sheffield, Ala., and Muscle Shoals, Ala., together with all government property and equipment belonging thereto, and the Waco limestone quarry in Alabama, together with Dam No. 2, and Dam No. 3, if and when constructed, and all their hydroelectric and operating appurtenances and accessories, should be dedicated for use in the national defense in time of war and for the production of fertilizers and other useful products in time of peace.

We are convinced that efficient and competent operation of the Muscle Shoals nitrate plants, together with the accessory plants which must be built and operated in connection with them, will soon lead to the general use of improved fertilizers at lower cost, and that such operation will increase rather than destroy the value of these plants for national defense.

We recommend the maintenance in operating condition of a large dependable nitrogen-fixation plant for national defense and a large production of improved and concentrated fertilizers by the continuous operation of present or improved plants at Muscle Shoals in active production by private enterprise under reasonable conditions that will encourage and promote the ends to be served and that at the same time will safeguard the public interest. If this cannot be done through a private lease, then plans for government operation should become effective within 90 days.

Recommendations

There should be definite limitations placed upon the power to be distributed from Muscle Shoals in order to protect the power supply for fertilizer manufacture, which is the primary purpose of the enterprise. We do not believe, however, that the hydroelectric properties at Muscle Shoals should be operated as isolated plants. This plan would not be economic, because the water supply, and therefore the power supply of the Tennessee River, is very variable, and a larger supply of power for all purposes would be made available by interconnecting these plants with the general distribution system of the southeastern States.

Since, in our judgment, the operation of the nitrate plants can best be accomplished and their benefits for the national defense and to agriculture can best be assured by considering and dealing with the properties so dedicated above as a unit, they should be leased as a unit and not as separate entities.

The conditions of the leasing of Muscle Shoals include the following:

That the lessee shall be required to manufacture nitrogen and other commercial fertilizers or concentrated ingredients for commercial fertilizers or both, either mixed or unmixed, and with or without filler, on the property covered by the lease or at such other plant or plants as the lessee may construct, using the most economical source of power available. The annual tonnage of these fertilizers or fertilizer ingredients supplied shall contain nitrogen, phosphoric acid, and potash, amounting in the aggregate to at least 18,000 tons after the third year, of which at least one-third shall be nitrogen, and said aggregate after the fourth year shall be progressively increased up to a maximum of 70,000 tons in the tenth year of the lease period, of which at least one-third shall be nitrogen, but the lessee shall be required to meet the commercial demand for his fertilizer products up to a nitrogen capacity equal to the full capacity of nitrate plant No. 2 as rapidly as he reasonably may be able to do in conformity with the commercial demand.

That there should be a limitation placed on the amount of profit to the manufacturer, which should not exceed 8 per cent on the fair annual cost of production.

That the lessee shall agree to determine by research whether or not, by means of electric furnace methods and industrial chemistry, there may be produced on a commercial scale fertilizer compounds of higher grade and and at lower prices than farmers and other users of commercial fertilizers have in the past been able to obtain, and if a process or processes are found which, in the reasonable judgment of the lessee, will reduce the cost of the fertilizer delivered to the farmer, the lessee shall reasonably employ such improved methods.

That the lease should in all cases be made only to American citizens.

We therefore unhesitatingly recommend legislation be enacted by Congress to lease this property on such terms as have been herein enumerated, and in event of failure to obtain a lease the President should have authority to cause these plants to be immediately operated as a government enterprise.

Minority Report

The minority report was signed by the two engineers of the commission, William McClellan and Harry A. Curtis. We do not have the space to print the minority report in full, as we should like to do, but give here as a matter of record the serious criticisms of the majority report and the recommendations of the minority. The balance of the minority report deals with a discussion of the power facilities of Nitrate Plants Nos. 1 and 2 and such fundamental considerations as the indispensability of private leases, the necessity of having separate power and fertilizer leases, the desirability of maintaining the nitrate-producing capacity of Plant No. 2 until such time as this reserve nitrate capacity is no longer required in national preparedness, an argument that the Muscle Shoals power should be used for the purposes named in the National Defense Act, that power should be reserved for fertilizer manufacture for a reasonable time to permit manufacturers to take advantage of it if possible, insistence that lessee construct storage dam commonly known as Dam No. 3, the point that the price of power at Muscle Shoals should be reduced as lower production costs are attained, and insistence that agencies for negotiation leases are necessary.

Criticisms

The Majority Report of the Muscle Shoals Inquiry submits a plan which is, in our opinion, open to a number of serious criticisms, amongst them the following:

1—It does not provide an incentive for the lessee to manufacture fertilizer at the lowest possible cost, for the profit is limited to a percentage of whatever the cost may be.

2—It does not provide with sufficient certainty that the possibility of applying the cheap Muscle Shoals power to fertilizer manufacturing will be thoroughly explored. The lessee is, to be sure, required to conduct research on this problem, but the commercial application of any successful methods discovered is optional with the lessee. Since he has no real incentive to cheapen fertilizer, and has, on the other hand, the greatest possible incentive to sell electric power in the highly profitable public utility market, there is no likelihood that successful methods will be discovered by the lessee, or applied if they do become available.

3—It fails to take into account the inevitable increment of revenue to the lessee as greater amounts of power become available at Muscle Shoals through regulation of the river. It does not preclude the possibility that a few years hence millions of dollars per year might be added to the income of the lessee at no cost to him save the small one of installing a few additional generating units in the existing power plants.

4—It insists that the power plants and the nitrate plants be leased as a unit, regardless of the fact that power generation and fertilizer manufacturing are utterly different propositions.

5—It provides for a certain yearly tonnage of fertilizer production by the lessee, and fixes the composition of this fertilizer within certain limits, without due regard to the market or the current fertilizer practices, without regard to what the actual requirements may be in the future, and without regard to the fact that the potential revenue from sale of power at Muscle Shoals will greatly increase as time goes on.

6—It provides that in case no private lessee can be found, (indicating that the proposed venture is deemed unprofitable) the Government shall operate the plants, a procedure which could only result in a waste of public funds with no permanent advantages to the farmer.

7—It does not insure that the cheap power available at Muscle Shoals be used for the purposes laid down in the National Defense Act, namely for manufacturing munitions in time of war, fertilizers and other useful products in time of peace. Under the plan of the Majority Report the Lessee could, and probably would, adopt chemical methods of fertilizer production requiring little power, and could then sell practically the whole output of power at Muscle Shoals without restrictions as to use, and at great profit to himself.

While there are many statements in the Majority Report with which we are heartily in accord, we cannot concur in recommending a plan which sacrifices so large a share of the potential values at Muscle Shoals and at the same time leaves the way open for enormous profits to a private lessee.

Recommendations

1—We recommend that authority be given by Congress to some agent of the United States to lease Wilson Dam and appurtenances, the hydro-electric power generating station thereat, and the steam-electric power generating plant at Nitrate Plant No. 2, all for a period not to exceed fifty years and under the terms and conditions outlined below.

2—We recommend the lessee be required:

(*a*) To maintain and operate the power plants, using the steam-electric plant as an auxiliary to the hydro-electric.

(*b*) To pay to the United States an annual rental for the power rights and properties a sum equal to 4 per cent of the fair present value of the properties, estimated to be $42,000,000.

(*c*) To deliver the power generated at Muscle Shoals as directed by the Muscle Shoals Board, provided, however, that any power not taken under the assignments of the Board may be sold by the lessee as hereinafter provided.

(*d*) To construct, at his own expense, whenever so directed by the Federal Power Commission, any part or all of a power and storage dam, with the power generating equipment, either at Cove Creek or at some other site approved by the Federal Power Commission; and to operate this dam so as to give the maximum useful effect at Muscle Shoals.

(*e*) To have the right, for a period of two years, to construct and operate Dam No. 3 with its power equipment, or, should the United States construct Dam No. 3, to have the right to lease the power at this dam.

(*f*) To make from time to time and at his own expense, such additions to the hydro-electric and steam-electric power generating equipment at Muscle Shoals as may be directed by the Federal Power Commission.

(*g*) To sell all power generated at Muscle Shoals at a price schedule agreed upon with the Federal Power Commission, except as otherwise directed by the Muscle Shoals Board under the authority vested in that Board, and provided, further, that should the lessee be unable to sell at the fixed schedule any of the power not taken under the assignments of the Muscle Shoals Board, then the lessee may sell such power at a less price, approved by the Federal Power Commission, deducting the difference from the rental to be paid the United States.

3—We recommend that all the power generated at Muscle Shoals be sold at the power generating station and at the same price to all customers, except as above provided; that the price schedule arranged between the lessee and the Federal Power Commission be adjusted triennially and be fixed so as to yield an annual gross income to cover the following: (*a*) Rental to the United States; (*b*) A reasonable return on such portions of the required investments of the lessee as, in the judgment of the Federal Power Commission, are properly chargeable to power production at Wilson Dam; (*c*) All actual operating and maintenance expenses and a fair remuneration; (*d*) Any taxes; (*e*) Reserve funds.

PERKIN MEDAL AWARD

At a meeting of the American Section of the Society of Chemical Industry on January 15, 1926, the Perkin Medal was presented to Richard B. Moore, general manager of The Dorr Company of New York City, in recognition of his work on radium, mesothorium, and helium.

Following introductory remarks by Harlan S. Miner, chairman of the section, Herman Schlundt gave his impression of Dr. Moore, the man, and S. C. Lind gave an account of the medalist's work. The medal was then presented by William H. Nichols and accepted by the medalist.

The Perkin Medal is awarded "annually to the American chemist who has most distinguished himself by his services to Applied Chemistry." It was founded in 1906 at the time of the Perkin semicentennial celebration of the coal-tar discoveries, the first medal being awarded to Sir William H. Perkin himself. The previous Perkin medalists are given below.

Date of Award	Awarded to	Principal Fields of Inventions
1907	Sir W. H. Perkin	Discoverer of first aniline color
1908	J. B. F. Herreshoff	Metallurgy; contact sulfuric acid
1909	Arno Behr	Corn products industry
1910	E. G. Acheson	Carborundum; artificial graphite
1911	Charles M. Hall	Metallic aluminium
1912	Herman Frasch	Desulfuring oil and subterranean sulfur industry
1913	James Gayley	Dry air blast
1914	John W. Hyatt	Colloids and flexible roller bearings
1915	Edward Weston	Electrical measurements; electrodeposition of metals; flaming arc
1916	L. H. Baekeland	Velox photoprint paper; bakelite and synthetic resins; caustic soda industry
1917	Ernst Twitchell	Saponification of fats
1918	Auguste J. Rossi	Development of manufacture and use of ferrotitanium
1919	Frederick G. Cottrell	Electrical precipitation
1920	Charles F. Chandler	Noteworthy achievements in almost every line of chemical endeavor
1921	Willis R. Whitney	Development of research and application of science to industry
1922	William M. Burton	Achievement in oil industry; efficient conversion of high-boiling fractions into low-boiling fractions
1923	Milton C. Whitaker	Great constructive work in field of applied chemistry
1924	Fredrick M. Becket	Process for extraction of rare metals from ores; manufacture of calcium carbide; processes for reduction of rare metals and alloys
1925	Hugh K. Moore	Electrochemical processes for caustic soda, soda and chlorine, production of wood pulp, hydrogenation of oils, etc.

Commercial Production of Radium, Mesothorium, and Helium

By R. B. Moore

Radium

THE element uranium is very widely distributed through the earth's crust, although it is usually found in relatively small quantities. In only a few localities is there sufficient concentration to give rise to commercial deposits. Since uranium is the mother of radium, radium also is very widely distributed in nature. The amount in ordinary sandstone, limestone, granite, etc., on account of the extremely sensitive methods of detection, can be quantitatively determined with ease.

Uranium minerals may be divided into two classes, primary and secondary. In the first class the radium is in equilibrium with the uranium, and therefore the mineral contains a maximum amount of radium in proportion to the amount of uranium. Secondary minerals are derived from the primary by solution and redisposition, and in many of these the radium is not in equilibrium with the uranium. Pitchblende is perhaps the best example of the first class and carnotite, autunite, and torbernite illustrate the second.

Pitchblende, an impure uranium oxide carrying traces of a number of metals as impurities, is found in Cornwall, Gilpin County, Colo.; St. Joachimsthal, Czecho-Slovakia; the Belgian Congo, etc., etc. It is soluble in sulfuric, nitric, and hydrochloric acids, and the mineral is readily decomposed by fusion with sodium carbonate.

Carnotite (a potassium uranyl vanadate) is found mainly in Colorado and Utah, where there are large deposits of low-grade material. These deposits have been the source, up to date, of more than 160 grams of radium element. The mineral is readily soluble in acids and is decomposed by boiling with sodium carbonate solutions or fusing with the solid.

Autunite, a calcium uranium phosphate, is found mainly in Portugal and Australia. It is soluble in acids and may be decomposed with sodium carbonate. Torbernite, copper uranium phosphate, is frequently found associated with autunite and is very similar to that mineral in its properties towards reagents.

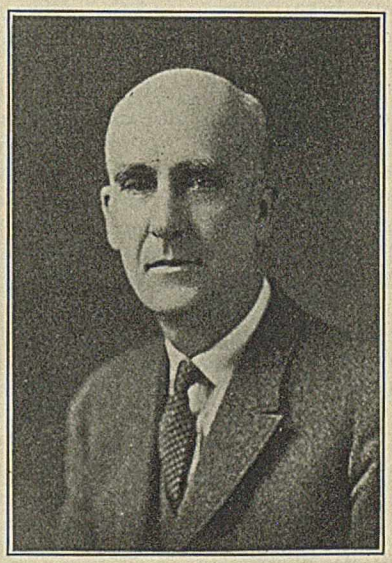
Up to 1912 the principal sources of radium were the pitchblende of Joachimsthal and the autunite of Portugal. From 1912 up to a few years ago the carnotite deposits of Utah supplied most of the world's radium. In 1922 the radium ores of the Belgian Congo were developed to the point of production. These consisted of pitchblende, curite ($2PbO$, $5UO_3$, $4H_2O$), dewindtite ($4PbO$, $8UO_3$, $3P_2O_5$, $12H_2O$), kasolite ($3PbO$, $3UO_3$, $3SiO_2$, $4H_2O$), soddite ($12UO_3$, $5SiO_2$, $14H_2O$), becquerelite (UO_3, $2H_2O$), stasite, and schoepite. These deposits are extremely rich, the selected ore which is sent to Belgium averaging nearly 50 per cent U_3O_8. On account of the extreme richness of the ore the Belgians have been able to compete favorably with producers dependent upon other sources of supply, with the result that only a relatively small amount of radium is now extracted outside of Belgium. The carnotite deposits of Colorado and Utah were considered extraordinary in the early stages of their development. In writing of them in 1913[1] the present writer said: "The United States possesses unique deposits in these carnotite ores. They constitute at present the largest supply of radium minerals in the world." Undoubtedly the radium deposits of the Belgian Congo are not only richer,

[1] *Bur. Mines, Bull.* 70.

but may be expected to provide an even larger amount of radium than the American ores.

Methods of Treatment

In selecting a method of treatment the metallurgist must decide first whether he wishes to put the radium in solution, from which it can be precipitated in a concentrated form, or leave the radium in the residue from which it may be extracted by a separate process. If it is decided to put the radium into solution, either hot concentrated sulfuric acid, nitric acid, or hydrochloric acid must be used. The great advantage of this type of treatment is that the radium can at once be precipitated in a concentrated form by diluting the acid and adding a small amount of sulfuric acid (if this has not been used) or sodium sulfate and barium chloride. The radium-bearing sulfate thus produced always represents a concentrate which can be easily treated for the recovery of the radium. Other methods, which leave the radium in the residue after the first treatment, call for a second treatment during which it is necessary to handle an amount of material almost equal to that during the first stage. On the other hand, the use of strong acids is inconvenient and requires special equipment. In addition, with hydrochloric acid the ore must contain extremely small quantities of sulfides or sulfates, as otherwise the radium extraction is not good. The amount of sulfates present in an ore when treated with nitric acid may be appreciable without seriously affecting the extraction. With sulfuric acid the presence of sulfates is immaterial.



R. B. Moore

Concentrated Sulfuric Acid

Boiling concentrated sulfuric acid dissolves radium salts readily. Most uranium ores are also decomposed by this treatment. After solution the hot acid is filtered through an iron suction or pressure filter. It is necessary for filtration to take place rapidly; otherwise, if the solution cools before filtration is completed some of the radium is reprecipitated. The strong acid filtrate is diluted below 10 per cent concentration, and preferably below 5 per cent, and allowed to cool. Barium chloride is then added in an amount requisite to give the proper concentration of the radium barium sulfate desired. Some radium is still held in solution by cold 10 per cent acid, and if the concentration is allowed to remain above this point the loss of radium may be considerable. It is safer to dilute down to 5 per cent.

The solution is filtered from the radium barium sulfate. The iron and calcium may be separated by boiling with excess of sodium carbonate, which precipitates them as carbonates, the uranium going into solution as the double carbonate of sodium and uranium.

The objections to this method are those that are attendant on handling hot concentrated sulfuric acid. The fumes are extremely unpleasant and the work has to be carried out in a building open on all sides. Filtering under such conditions is extremely difficult and the pressure filter is probably the most satisfactory method. If the ore is low grade the tonnage of acid required is correspondingly large and the difficulties are greatly increased. Generally speaking, this is not a method to be recommended.

Dilute Sulfuric Acid

Most uranium ores are decomposed by hot dilute sulfuric acid. Minerals such as carnotite, autunite, and torbernite are very soluble, and pitchblende is also soluble, but with much more difficulty. The radium necessarily stays behind with the residue, and therefore this method is more applicable to high-grade ores, as otherwise the concentration of the radium obtained by the first step is not great. A second treatment to obtain a further concentration of the radium is always necessary before it is ready for refining. This in the case of carnotite usually consists of a sliming process in which the residue is agitated in water, the sands allowed to settle out, and the fine material slimed off into a separate tank. This slime contains most of the radium sulfate. The method used by one plant was as follows: 1000 pounds of ground ore were treated with 700 pounds of dilute sulfuric acid and 50 pounds of commercial hydrochloric acid in a lead-lined wooden tank. The mixture was boiled with live steam for one hour, the heavy sands allowed to settle, and the slimes decanted with the acid liquors. The sands were then washed with water by decantation and discarded. The liquor and slimes were allowed to stand for 4 days, after which the slimes were separated by filtration.

These were boiled with a mixture of soda ash and caustic soda, five times as much soda ash as caustic being used. After filtration and washing the soluble carbonates were leached with sulfate-free hydrochloric acid, the radium being recovered in the usual way by fractionation. The uranium and vanadium were precipitated out of the sulfuric acid solution with lime, from which they were later recovered by one of the standard methods. This particular "sliming" method gave rather low costs. Care must be taken, however, that in the decantation of the slimes they are really separated from the sands, which are discarded.

The sulfuric acid method is used at Oolen in Belgium, where the fine plant of the Union Minière de Haute Katanga is situated. The process varies from others on account of the high-grade ores treated. Whereas, from 300 to 400 tons of carnotite must be treated in order to obtain 1 gram of radium, at Oolen less than 10 tons are required for this amount of radium. This allows a plant arrangement and design which is not possible in other places, the equipment of the plant having been described as being more like a fine kitchen than an actual metallurgical plant. All agitators are mechanical. All fumes are carried through large steel collecting boxes and from there to a stack 125 feet high. A large acid tank holding sulfuric acid is suspended at the top of the building, from which it flows by gravity into the necessary containers and tanks. Pumps are located on the lower floor, as are catch boxes for filter presses, etc. The first treatment, by moderately dilute sulfuric acid, decomposes the mineral and dissolves the uranium, iron, and traces of copper, etc., leaving the radium in the residue. This is followed by treating with a sodium chloride solution in order to dissolve the lead left in the residue which is afterwards recovered. This residue is then given the usual sodium carbonate leach in order to convert the radium into carbonate. After thorough washing the residue is treated with dilute C. P. hydrochloric acid, which decomposes the radium carbonate and gives the usual radium solution, from which the rare element is precipitated by barium chloride and a little sulfuric acid. Whereas, a sulfate obtained from carnotite usually carries from 0.5 to 1 mg. of radium per kilogram, the concentrate obtained at Oolen averages 7 mg. per kilogram.

All residues are stored for further use if possible in connection

with the recovery of other radioactive elements. The amount of residue is small, owing to the richness of the ore, 18 tons of ore actually treated giving a residue that would fill only two 50-gallon barrels.

The treatment of such a large amount of high-grade ore is particularly favorable for a study of methods of recovery of such elements as actinium and polonium. It also allows the recovery of considerable quantities of radio-lead.

The filtrate from the sulfuric acid treatment contains the uranium, which is purified in the usual way by precipitating the iron, calcium, etc., with excess of sodium carbonate and the uranium in the filtrate as sodium uranate.

This factory began to produce radium in August, 1922, and from that time until the following January their total production was more than 15 grams of radium element. In the following year[2] it is stated that the production averaged 4 grams per month. The Belgians are very loath to give any detailed information concerning their technical methods of production and just what the total production has been up to date is not known. On the basis of 4 grams a month it would be possible for them to produce up to the end of 1924, 110 grams of radium element. It is not believed, however, that so much production has been actually obtained, because there has not been a sufficient market for this amount. On the other hand, it is claimed that considerable stocks have been accumulated. Up to the present, something like 165 grams of radium have been produced from American carnotites, so there is at least a possibility of a total production up to date for the whole world of over 300 grams of radium element, although this figure is probably high.

Hydrochloric Acid

Leaching with hydrochloric acid was one of the first methods used on carnotite, autunite, and other acid-soluble ores. When the ore is almost entirely free from sulfates the extraction obtained is fairly good with moderately concentrated sulfate-free acid, extractions as high as 86 or 87 per cent being obtained under very favorable instances on carnotite. On the other hand, if 2 or 3 per cent of gypsum is present in the ore, extractions as low as 50 per cent, or even less, may be obtained. The use of hydrochloric acid, therefore, cannot be recommended.

One rather interesting exception to this rule was in connection with the plant that was operating for several years in order to supply radium to the Radium Institute in London. This plant operated on Cornish pitchblende and it was found possible to decompose the ore and leach out the radium in moderately concentrated, cold, sulfate-free hydrochloric acid. Between 2.5 and 3 grams of radium bromide were produced in this manner before the War.

Nitric Acid

Nitric acid has two advantages: it decomposes the uranium ores very readily, pitchblende going into solution much more rapidly than in hydrochloric or sulfuric acids; and, in addition, the radium goes into solution instead of remaining in the residue and can then be precipitated as a high-grade concentrate with barium chloride and sulfuric acid. The additional cost of nitric acid over sulfuric at first makes this process look impossible in comparison. On the other hand, if sodium nitrate can be recovered with small loss and nitric acid be once more made from the sodium nitrate, a cycle is obtained that reduces the cost of nitric acid to a figure as low as, if not lower than, the cost of hydrochloric acid. In addition, it eliminates entirely the sliming step and the subsequent treatment of the slime necessary in connection with the dilute sulfuric acid method.

The solvent action of nitric acid on radium sulfate is much greater than that of hydrochloric acid. This greater solvent action was the general basis for the method devised by the writer in the Bureau of Mines and used in the plant of the National Radium Institute.

The ore was ground to 20 mesh and leached with strong hot nitric acid in earthenware pots. The amount of acid used was 121 pounds of 100 per cent nitric acid to 500 pounds of ore, the acid being diluted to 38 per cent strength, ore high in sulfates sometimes requiring stronger acid. The acid was brought near the boiling point by steam, the ore being stirred with a wooden paddle. After solution of the uranium, iron, etc., the whole was dumped on an earthenware suction filter and filtration was carried out as rapidly as possible, the residue being washed first with hot dilute acid and finally with distilled water. The filtrate was brought as near to the neutral point as possible with sodium hydroxide without precipitating the dissolved metals and the radium was then precipitated in the usual way with barium chloride and sulfuric acid. After standing 3 days the clear liquor was decanted into a tank containing an excess of boiling sodium carbonate, where the iron, calcium, and most of the aluminium were precipitated and the uranium and vanadium went into solution as the double carbonate of uranium and sodium and as sodium vanadate. After filtering from the precipitated iron, calcium, etc., the sodium carbonate solution was nearly neutralized with nitric acid and sodium hydroxide was added until complete precipitation of sodium uranate was obtained. The hot filtrate was completely neutralized with nitric acid and ferrous-sulfate was added to the agitated liquid in order to obtain iron vanadate, which was filtered and washed. The filtrate contained sodium nitrate and a small amount of sodium sulfate. The whole was evaporated in iron tanks heated by steam coils immersed in the solution. After concentration the solution was run into steel crystallizing pans, where the sodium nitrate was crystallized out and used in the making of nitric acid. About 85 per cent of the acid used was recovered as sodium nitrate.

Under the coöperative arrangement between the U. S. Bureau of Mines and the National Radium Institute, 8.5 grams of radium element were produced by this method. The total net cost for this production, after the plant was sold and including the time and expenses of the government men, was $340,000. Over 60,000 pounds of 95 per cent uranium oxide were produced at the same time and the costs for such production are included in the above figures. This oxide was not sold at the time the partnership was dissolved, but considerable amount has been disposed of since at various prices. If the whole 60,000 pounds were sold for $1 a pound, it would reduce the net cost of the radium to $280,000, or a cost of less than $34,000 per gram of element.

In a recent article[3] it has been stated that the American Government tried to monopolize the radium industry; it was also intimated that the plant of the National Radium Institute was shut down because it was not successful. Both statements are absolutely incorrect. The plant was closed when as much radium had been produced as was needed.

The objections to the nitric acid method are that it will not treat any uranium ore with equal facility. The extraction is poor on a pitchblende high in pyrites such as the mineral found in Gilpin County, Colo. In addition, if carnotite or similar mineral contains more than 2 per cent gypsum, the extraction is not good; with carnotite containing 1 per cent gypsum or less the extraction may go as high as 95 per cent, and with ore of this character it is undoubtedly one of the best methods yet devised.

Alkaline Leach

One of the most popular methods of treating ores such as carnotite and autunite is by an alkaline leach. This consists of boiling the ore with a solution of sodium carbonate either at atmospheric pressure or in an autoclave. The cost of treating

[2] Matignon and Marshall, *Chimie & industrie*, 14, 355 (1925).

[3] *Chimie & industrie*, 14, 67 (1925).

in an autoclave is decidedly greater than at atmospheric pressure, but the conversion of radium sulfate into radium carbonate is more complete, and the time required is less. The barium and calcium sulfates in the ore are at the same time converted into carbonates. Autoclaving with sodium carbonate is an excellent method of treating fairly high-grade ore containing minerals of the type indicated above. It is too expensive to use on low-grade material and is not a practical method for pitchblende, as such treatment has very little effect on that mineral. A considerable portion of the carnotite treated in the past has been handled by a sodium carbonate leach, during the first few years of the industry the heating being done at atmospheric pressure. Armet de Lisle used this method with success on autunite ores from Portugal. It was also used for a while by one or two companies in this country. Later the advantages of the autoclave were recognized by the Radium Company of Colorado.

Their method was as follows: After grinding the ore to about 20 mesh it was mixed with from 16 to 25 per cent of its weight of soda ash. For the average run of carnotite 16 per cent was sufficient, but ores high in organic matter required up to 25 per cent of soda.

The mixture was placed in cylindrical autoclaves with a cone bottom. These autoclaves could easily handle from 1000 to 1200 pounds of ore at a charge. Steam under pressure was introduced at 90 to 100 pounds. No agitating device was necessary as the live steam was sufficient. The ore was left under pressure for a period of from 4 to 8 hours, depending on its grade, impurities present, etc.

After the preliminary treatment was finished, the pressure was reduced to 50 pounds, and as the autoclaves were connected directly with filter presses, the charge was forced into the press from the autoclave. The alkali filtrate was pumped into a storage tank for treatment for vanadium, etc. Sulfate-free water was used for washing the filter cake.

This was then ready for leaching with dilute hydrochloric acid in small stoneware pots taking 165 pounds of carbonate ore each at a charge. The total capacity was 7 tons per day.

After boiling thoroughly for an hour by means of live steam, the ore and acid were discharged into a wooden tank beneath, where after settling for a few minutes the solution and slimes in suspensions were siphoned off into another tank. Sulfate-free water was then added to the sands, which were thoroughly stirred up with steam and the liquor and any additional slimes were siphoned off. Two or three washings were sufficient to clean the sands to a point where the radium contained was less than an equivalent of 0.1 per cent U_3O_8. The sands comprised about 90 per cent of the weight of the ore, while the soluble material and slimes together represented the other 10 per cent. This method involved the separation of the radium in two forms; the larger part going into solution in the hydrochloric acid, and a small amount of unconverted salts remaining in the slimes in a reasonably concentrated form ready for additional treatment.

These slimes were allowed to settle and the supernatant liquor was siphoned off into a tank where radium barium sulfate was precipitated in the usual way.

Sliming Methods

As already stated, a direct leach of the ore by means of sodium carbonate is an excellent method provided the grade of the ore is over 2 or 2.5 per cent U_3O_8. If the ore is of poor grade there is considerable advantage in making a preliminary concentration of the radium by some cheap method which extracts the vanadium, uranium, etc., but leaves the radium in the insoluble form in the residue. As the radium is usually found in the fine material in the ore and not in the coarser silica grains the desired concentration can be obtained in carnotite and other similar ores by separating the fine material from the coarse by means of "sliming" methods. This idea was partly covered in the method described above used by the Radium Company of Colorado. Since the slimes usually represented from 10 to 20 per cent of the total ore, a very much smaller amount of material was actually treated in order to convert the radium in an insoluble form into radium as carbonate and therefore acid soluble. The method used by one of the operating plants in the United States has been described by d'Aguiar.[4]

The ore, ground to 60 mesh, was placed in dissolving tanks made of acid-proof brick. These were shallow and were each about 60 square feet in area. The ore was spread in a layer from 4 to 6 feet in the bottom and thoroughly wetted with water or with a weak liquor containing small quantities of vanadium and uranium obtained from previous operations. Hydrochloric acid was added in quantity sufficient to dissolve all the uranium and vanadium, as well as the calcium, iron, etc. This quantity was determined by previous analysis of the ore. The ore was turned and agitated and sulfuric acid was then added in quantity sufficient to precipitate all the barium and calcium. Additional water was then added and the ore again stirred.

The liquor was removed by decantation through an opening in the side of the tank at a height flush with the top of the bed of sand tails. The latter was washed by adding more water, stirring, and again decanting. The liquor and first wash water went to storage, succeeding wash waters to a second storage tank to be used again in the first step of the process. The sand tailings were tested and dumped.

The liquor and slimes in the first storage tank were filtered through wood-frame filter presses using Duriron pumps. After thorough washing the slimes, which might be classed as a crude radium concentrate, were treated with sodium carbonate in autoclaves as already described. After a treatment of several hours, the mass was filtered through frame presses and the residue was leached in the usual way with sulfate-free hydrochloric acid and a high-grade radium concentrate obtained by adding to the acid liquor after filtering some barium chloride and sulfuric acid.

Another plant in this country varied the above treatment by using 700 pounds of dilute commercial sulfuric acid and 50 pounds of crude hydrochloric acid for every 1000 pounds of ground ore treated. The mixture was boiled with live steam for one hour and the heavy sands were allowed to settle and the slimes decanted off with the supernatant liquors. Instead of boiling with soda ash alone in an autoclave, this plant used a mixture of soda ash and caustic soda in the proportions of 5 to 1. It was believed that this gave a better concentration than soda ash alone, and this is probably true on some ores.

For low-grade ores amenable to this process the slime method is a good one, being economical and not requiring very specialized equipment. The principal objection to it is the large tank capacity required, as considerable time is needed for complete settling of the slimes. If plant space is a factor or if the ore is fairly high grade this method loses its advantages.

Fusion Method

When an ore is not amenable to any of the methods described above, it is necessary to resort to fusion methods. Radcliff[5] devised a method for the treatment of the complex radioactive ores of Australia, which contain tantalum, niobium, cerium, thorium, and other rare earths besides uranium. The crushed ore was fused in a reverberatory furnace with about 2.5 times its weight of acid sodium sulfate. After the charge was fused and while the mass was still fluid, sodium chloride (10 to 15 per cent of the weight of the ore) was added and well rabbled. The addition of the sodium chloride in the presence of fused acid sodium sulfate resulted in a powerful decomposing and oxidizing effect and changed any ferrous salts to ferric. The fused product was tapped from the furnace, cooled, crushed, and

[4] *Chem. Met. Eng.*, **25**, 825 (1925).

[5] U. S. Patent 1,049,145.

turned into vats containing warm water, which was agitated. Most of the uranium, iron, rare earths, and a part of the tantalum and niobium went into solution. The radium remained in the form of insoluble radium sulfate and was in suspension; the liquor and fine insoluble material were "slimed" off, allowed to settle in the usual way, and filtered. The crude radium concentrate thus obtained was treated by the regular methods.

The earlier method of treating the pitchblende obtained at St. Joachimsthal was by fusing with sodium sulfate, the uranium being thus changed into sodium uranate, which can be dissolved by means of dilute sulfuric acid, the radium remaining in the residue. Before the discovery of radium this residue was considered to be a waste product and was thrown away. The extraction of the radium from the accumulated residue is described by Haitinger and Ulrich.[6] This involved leaching with caustic soda, washing, and treating the residue with 1:1 hot crude hydrochloric acid to remove lead, polonium, actinium, etc. Crystals of lead chloride were formed on cooling and the polonium and actinium were precipitated by means of ammonium hydroxide, in the filtrate. The residue from the treatment with hydrochloric acid was boiled in a solution of sodium carbonate, and from that point on the treatment was the usual one for the conversion of radium barium carbonates into chlorides.

For a number of years past the process at the plant at St. Joachimsthal has been somewhat different. The fusion method is still used, but the concentrates or ore, which are high grade averaging around 50 per cent U_3O_8, are fused with soda ash and a small amount of sodium nitrate. This decomposes the ore and converts the radium directly into carbonate. After leaching and washing, the uranium is in the filtrate as double carbonate of sodium and uranium, and the radium is in the residue as carbonate, which can be leached with dilute sulfate-free hydrochloric acid according to the usual procedure.

Fusion methods are not economical except on high-grade ores. Pitchblende is not easily decomposed by acids and is affected only slightly by boiling with sodium carbonate solution; therefore fusion methods are well adapted for this ore. The mixture of soda ash and sodium nitrate is probably better than any other that has yet been devised.

Barker and Schlundt[7] in a very excellent monograph have tested out most of the suggested methods of treatment on five analyzed carnotite ores from Colorado and Utah. Table I gives a partial analysis of the ores used.

Table I—Analysis of Carnotite Ores
(Per cent)

	Temple Mt. No. 1	Temple Mt. No. 2	Long Park	San Rafael	Polar Mesa[a]
Loss of weight on ignition	11.50	18.15	3.94	6.03	3.61
Silica (SiO_2)	77.44	62.03	81.32	69.54	81.21
Iron and aluminium as oxides	5.15	7.84	7.94	10.62	5.01
Calcium as sulfate	0.54	2.64	1.49	0.02	2.57
Barium as sulfate	0.03	0.08	1.76	0.01	0.15
Vanadium as V_2O_5	2.45	3.51	3.50	6.45	4.03
Uranium as U_3O_8	1.49	2.68	1.27	3.21	2.04

[a] This ore is rather unique in that the quantity of carbonates contained is comparatively high, which accounts for the marked effervescence when acid is added.

The two samples of ore from Temple Mountain have a high loss on ignition and contain an appreciable amount of organic matter. The Polar Mesa ore contains some carbonates not indicated in the analysis. Table II represents the final percentages of radium recovered by different methods.

Table II—Radium Recovered from Carnotite Ores (Barker and Schlundt)
(Per cent)

Method	Temple Mt. No. 1	Temple Mt. No. 2	Long Park	San Rafael	Polar Mesa
HNO_3 direct	55.3[a]	59.5	94.6	91.5	93.2
HCl direct	...	...	89.7	50.0	78.5
Carbonate conversion	83.8	69.0	86.4	86.0	...
HCl sliming	80.9[a]	69.4	85.1	78.7	78.7
Dil. H_2SO_4-sliming	76.5[a]	76.0	83.8	82.1	82.2
Conc. H_2SO_4-sliming	75.0	73.8	80.6	74.7	...

[a] Values are for per cent extracted rather than for per cent recovered.

[6] *K. K. Akad. Wissenschaft*, **117**, 619 (1908).

[7] University of Missouri, *Bull.*, Vol. **26**.

It can be readily seen that the nitric acid method gives the highest extraction of all except the Temple Mountain ore. The low extraction on that ore is undoubtedly due to the presence of organic material. The carbonate conversion and the sliming method give the best average results, but do not give so high an extraction as the nitric acid method on ores which are amenable to that process.

Therefore, in treating any radium ore, the process to be selected should be dependent upon a number of "factors" and the selection should be determined entirely by these "factors." The type and grade of ore, the cost of chemicals, the plant space available, and time desired for complete cycle, the recovery obtained, etc., all have to be considered carefully. The question of recovery is more important in connection with radium ores than possibly any other ore that the metallurgist has to handle. A few per cent extra recovery will pay for a considerable amount of extra equipment, chemicals, or labor.

Refining of Radium

Treatment of Crude Sulfates

The crude sulfates may vary widely in radium content, from 0.25 mg. of radium per kilogram containing an appreciable amount of silica and other impurities to a high-grade sulfate from pitchblende carrying as much as 5 or even 6 or 7 mg. of radium, calculated as element, per kilogram. The preliminary treatment is very largely the same in each case. If too much silica is not present the sulfate may be reduced in a large graphite crucible with charcoal, as was done by the Bureau of Mines in the plant of the National Radium Institute in Colorado. The sulfate is mixed with one-fifth its weight of powdered charcoal and heated for 7 or 8 hours in an oil or other suitable furnace at a temperature of 800° C. The sulfate is reduced to sulfide, and on cooling the radium barium sulfide is removed and broken up. This is dissolved in dilute C. P. hydrochloric acid. If appreciable quantities of silica are present the per cent reduction in the furnace is greatly reduced. For high-grade sulfates this is an excellent method. The portion insoluble in the acid consists of undecomposed radium barium sulfate, a small amount of charcoal, and some silica. The amount of radium in this residue is usually about the same as that in the original sulfate, and such residues are, therefore, stored and retreated in the same manner. A third residue is also obtained. There is a tendency for the accumulation of lead in the second and third residues, and, therefore, it is better to fuse the third with sodium carbonate than to reduce it again with charcoal. During the carbonate fusion most of the lead is eliminated as metallic lead.

Another method, which is perhaps more commonly used, is boiling with a strong solution of sodium carbonate in excess. This may be done at normal pressure or preferably in an autoclave. In the latter case the conversion is excellent and the improved results are worth the additional equipment. The residue is leached with dilute hydrochloric acid and the barium radium carbonate is thus dissolved. The unconverted portion is either accumulated separately and retreated or is added to a fresh batch of sulfate. If the sulfate concentrate is very high grade, containing 3 or more milligrams of radium element per kilogram, it is usually preferable to dissolve the converted carbonates directly in hydrobromic acid instead of hydrochloric, thus starting the fractionation series with bromides instead of chlorides. If the sulfates are less rich, on account of the cost of hydrobromic acid it is preferable to start fractionation as chlorides and get a preliminary fractionation before the chloride series is converted to the bromide.

The advantage of fractionating as bromide instead of chloride is due to the difference in the crystallization factor of the salts. That of radium-bearing chloride in hydrochloric acid is about 1.5 whereas that of the bromides in hydrobromic acid is about 2. This means that in the first case if half of the barium chloride

is removed there will be 50 per cent more radium in the crystals removed than in the liquor left behind. With the bromides the amount will be double. It therefore takes a considerably larger number of fractions in a chloride than in a bromide series to obtain a definite concentration.

Some other methods have been suggested. H. N. McCoy proposed and used the hydrates. In this case the radium tends to concentrate in the mother liquor instead of in the crystals. One of the objectionable features in connection with this method was that all of the solutions had to be kept on ice during crystallization and it was inconvenient in other ways.

Fractionation

The radium barium chlorides obtained from the sulfates are concentrated in a suitable vessel. Steam-jacketed kettles made of silicon-lined acid-proof ware are excellent and are easy to manipulate. Those who do not care to go to that expense either use very large porcelain evaporating basins, which are inconvenient, or large earthenware vessels, immersed in a bath of boiling water. The barium chloride solution in the first vessel is evaporated to such a concentration that on cooling one-half of the barium chloride crystallizes out. The liquor is siphoned into the next evaporator in the series and the process repeated, one-half of the remaining barium chloride being allowed to crystallize. This procedure can continue all the way down the series.

After a continuous series has been established, fresh liquor may be introduced each day in the "zero" evaporator, the crystals going in one direction getting richer and richer in radium and the solution going in the other direction getting poorer in radium, until after three or four crystallizations on the "minus" side it is discarded.

The usual fractionation scheme is to move the crystals from a "minus" evaporator into the next one higher in the series, where it meets the liquor from the next one higher up. The aim is to get the radium concentration of the mother liquor and the crystals that are mixed as nearly the same as possible. Some operators vary this method to some extent, by changing the ratio of the quantity of crystals to mother liquor in given evaporators in order to obtain the above desired results. The bulk of crystals rapidly decreases as the concentration increases, and after two or three crystallizations on the plus side in the plant the crystals are transferred to the laboratory. At some point in the series, depending entirely upon the richness of the crystals, the chlorides are converted into bromides. Before doing this, however, the last trace of lead should be removed by passing hydrogen sulfide through the solution to which ammonium hydroxide has been added. Although the solution is actually alkaline, the loss at this point is not more than 0.2 per cent and the precipitates are saved for further treatment. The radium can easily be recovered and the lead represents the radio-lead obtained from the crude sulfates. Under normal conditions of operation this radio-lead is contaminated by ordinary lead, unless C. P. sulfuric acid is used throughout the plant. The chlorides can best be converted into bromides by precipitating the radium and barium with ammonium carbonate in slight excess. After thoroughly washing the carbonates are dissolved in hydrobromic acid.

The bromides are fractionated in the same way as the chlorides, and it is not difficult to obtain quickly a high-grade salt. Starting in the plant with a concentrate containing 1 mg. radium per kilogram, ten or twelve bromide fractionations will give a product containing from 1 to 2 per cent radium bromide. When a sufficient amount of this grade material is collected, a fresh fractionation series is started every month or two and the 1 or 2 per cent is quickly stepped up to 50 or 60 per cent, or more. The Bureau of Mines on one occasion for scientific purposes produced over 100 mg. of 100 per cent radium bromide without a great deal of trouble. At the time the Bureau of Mines carried on its work in Colorado, radium salts had been fractionated by a number of persons abroad, but no real details had been published that were applicable to regular plant procedure. The same statement applies as regards radium measurements. Methods which were quite satisfactory for purely scientific purposes were not at all satisfactory for plant control, and the bureau operators found themselves in the position of carrying out a series of research experiments with large quantities of very valuable material with extremely unsatisfactory methods of control. These had to be developed and were published. In the end the difficulty of refining radium was less than was anticipated, but until the details were worked out it was natural under the circumstances to assume that they were greater than they actually were. Full details of the refining of radium and methods of measurement have been fully described in a number of publications.[8]

Mesothorium

Next to radium mesothorium is the most important of the radioactive elements, since its disintegration products emit the three types of radiation that are associated with radium and its disintegration products—namely, alpha, beta, and gamma rays. Since its life period is reasonably long, it can therefore be used as a substitute for radium. It is particularly applicable in the making of luminous paint for watch dials and other purposes, and its use in this industry has conserved a good deal of radium for medical purposes.

Mesothorium is the first product of the disintegration of thorium and is therefore always found in thorium minerals. The Bureau of Mines recognized the importance of the recovery of this element in the manufacture of thorium nitrate from monazite, and made arrangements with the Welsbach Company through H. S. Miner for a coöperative research, which resulted in a process which has been successfully used by the Welsbach Company in the recovery of mesothorium.[9]

Helium

When Professor Moureau of Paris was at the Disarmament Conference in Washington, he stated at a luncheon that "if any one had told him five years before that helium would be put in airships he would have considered it in the same light as if some one in his audience told him that the Washington Monument was going to be covered with diamonds." If this undertaking is really of so much importance it is perhaps well to review its commercial history before taking up strictly technical matters.

Commercial History

In 1914 a German Zeppelin was attacked by allied airplanes and, although pierced by numerous incendiary bullets, for some unknown reason it did not catch fire. This gave some one in the British Admiralty an idea that the Germans had developed a noninflammable gas which was being used in airships. The matter came to the attention of a number of scientific men in England and Richard Threlfall, now Sir Richard Threlfall, conceived the idea that the Germans had acquired a new source of helium and had filled the airship with this rare gas.

Threlfall wrote the British Admiralty and the latter became interested at once. They authorized Sir Richard to make a report on possible sources of helium and he was later joined in his work by Sir William Ramsay. It was curious that they did not seem to know of the work of Cady and McFarland on the natural gas of Kansas. At any rate "blowers" of fire damp in coal mines were analyzed with the hope of getting a sufficient

[8] *Bur. Mines, Bull.* **103**, **104**, etc.

[9] Schlundt, *Bur. Mines, Tech. Paper* **265**.

supply of helium. This hope was based on the "blower" at Anzin, which lasted for twelve years and liberated about 4000 cubic meters of helium per annum. A similar one at Frankenholz gave rise to nearly as much helium as that at Anzin. In a memorandum in December, 1914, Sir Richard Threlfall first mentioned the work of Cady and McFarland. In February, 1915, and in the following spring he reported to the director of the Air Department information which had been received concerning the natural gas wells of Kansas. As a result the British Admiralty appropriated a small sum of money, which was allotted to Prof. J. C. McLennan, of the University of Toronto, for an investigation of the natural gas supplies of Canada and for experimental work on the recovery of helium from natural gas.

In February, 1915, Sir William Ramsay wrote to the writer that the British Admiralty was much interested in possible sources of helium which might be utilized for its commercial production. He emphasized the great advantage that airships filled with helium would have over those containing hydrogen, but stated that he had little faith personally in airships, even though they contained helium. He did not mention Sir Richard Threlfall's connection with the work or outline the Admiralty plans.

The importance of Ramsay's suggestion was at once recognized on account of the work of Cady and McFarland, and as the United States was not at war nothing was done until this country actually did enter the World War. In April, 1917, at a meeting of the American Chemical Society in Kansas City, a paper was given by C. W. Seibel, of the University of Kansas, on the presence of the rare gases in certain natural gas supplies of Kansas and other states. In the discussion which followed the writer referred to the interest of the British in helium for airships and stated that in his belief such a program was practical and as the United States was now in the war it should be carried out. Up to this time no further information had been obtained concerning the operations of the British nor was it known that the Canadians were also interested. The only contact had been through the letter from Ramsay mentioned above and the information contained was in one short paragraph.

Shortly after the meeting in Kansas City, G. A. Burrell, of the U. S. Bureau of Mines, heard through L. W. Lidbury, who had recently returned from England, of the interest in helium among the British, and in the following June, when the writer was in Washington, the possibility of the cheap production of helium from natural gas was discussed and the writer and Mr. Burrell interviewed Col. Chas. deF. Chandler, in charge of the Balloon Division of the Army. Colonel Chandler showed a keen appreciation of the story told him and stated that the Army would be much interested in the investigation. Colonel Chandler felt that anything that would give the United States an advantage over the enemy in time of war should not be overlooked simply on account of greater cost. This interview represented the real concrete starting of the commercial production of helium in the United States and concerning it Colonel Chandler wrote under date of December 19, 1923:

> It was one day in June of 1917 that you and Dr. Burrell called at my office, presumably because I was at that time in charge of the Balloon Division of the Aviation Section of the Signal Corps. You told me of helium being one of the constituents of natural gas in the central part of the United States, adding remarks about its characteristics that would make it superior to hydrogen for military balloons provided suitable extraction processes could be developed. I was then asked whether the Signal Corps desired helium sufficiently to encourage development of the extraction processes by allotment of funds for the purpose.
>
> My personal opinion was that it should be done, even though the cost would be considerably more than hydrogen, for the reason that anything that would give us an advantage over an enemy in time of war ought not to be overlooked simply on account of greater cost. This matter involved new policy and would surely require a greater expenditure of funds than amounts subject to my approval, therefore, I agreed to confer promptly with the Chief Signal Officer of the Army, which was done within a few hours. General Squier was much interested in the proposal and instructed me to present the matter to the Aircraft Production Board at its next meeting a day or two later; that board was responsible for decisions regarding aircraft policy affecting both the Army and Navy. The questions asked by members of the board indicated a favorable interest and I was directed to secure approximate estimates from the Bureau of Mines of the funds required for developing a practicable extraction process.

There followed a number of conferences in the Bureau of Mines, and it was decided that the production was feasible but difficult and in order to have a possible chance for success all the best methods of liquefaction were needed, and, therefore, three experimental plants should be constructed rather than one. Therefore, the Linde Air Products Company, the Air Reduction Sales Company, and the Jeffries-Norton Company were asked to coöperate with the Government and developments finally culminated in a recommendation on July 26, 1917, by the Aircraft Production Board of an allotment of $100,000 in equal shares from Army and Navy appropriations to make helium available as a substitute for hydrogen in balloons and airships. It was further recommended that arrangements be made with the U. S. Bureau of Mines to carry out the undertaking. This recommendation was approved. At first Mr. Burrell was placed in charge of the work by Van H. Manning, director of the bureau. About this time Capt. R. B. Owens of the Signal Corps went to England on a special mission taking with him a letter from Mr. Burrell which he presented to the British Admiralty. This led to the dispatch to this country of Comm. C. D. Bridge and Lt. Comm. S. R. Locock as a commission on behalf of the Admiralty to canvass the helium situation in the United States and investigate methods of production. From these officers we obtained for the first time definite information regarding the activities of the British Government in connection with helium. Their visit greatly stimulated interest in our helium work in certain quarters and undoubtedly encouraged the British Admiralty to go ahead with their small-scale experimental work in Canada through Professor McLennan. From that time on the two countries kept in contact and in May, 1918, Professors Satterly and Patterson of Canada visited the United States in order to inspect our plants.

Immediately Mr. Burrell made a quick survey of the best localities for locating the experimental plants. From a record of analyses printed by the U. S. Bureau of Mines[10] he found that the natural gas from the Petrolia, Texas, field contained natural gas of over 30 per cent nitrogen. Cady and McFarland had previously shown that there was a very decided connection between the helium and nitrogen content of natural gas. Samples were therefore sent to Dr. Cady and to the writer for analysis, and results showed that the Petrolia gas contained over 0.9 per cent helium. As the field was suitable in other respects, it was decided to locate the plants in Texas, two at Fort Worth and one at Petrolia, at the source of the gas supply. The work in connection with the helium undertaking at this time assumed such proportions and broadened so much that Mr. Burrell felt on account of his chemical warfare work that he would be unable to carry it on properly and, therefore, resigned. Prof. W. H. Walker was then put in charge for a short time. Following him Dr. Cottrell handled matters in the Bureau of Mines under Dr. Manning and Mr. P. McBiddison in the field. The Linde and Air Reduction plants were constructed by their engineers under the general supervision of the Bureau of Mines and the Jeffries-Norton Plant was built under the direct supervision of the bureau.

Owing to difficulties which developed in connection with the organization, in June, 1918, the director of the bureau assigned the writer as his personal representative in the field with full charge of all matters pertaining to helium outside of Washing-

[10] *Tech. Paper* **109**.

ton. This included general charge of the three experimental plants and all other matters connected therewith. He remained in intimate connection with the helium work until October 1, 1923, several months after his resignation from the Bureau of Mines.

In order to coördinate all of the different agencies concerned in the helium project, and in order to take steps for controlling matters connected with the exploration and conservation of helium, a committee consisting of one representative of each of the three governmental departments was appointed on August 28, 1918—G. O. Carter, chairman, represented the Navy; H. N. Davis, the Army; and G. O. Orik, the Department of the Interior. Later, Mr. Carter was succeeded by Comm. A. K. Atkinson, who in turn was succeeded by Comm. S. A. Kraus and Capt. E. S. Land. Dr. Davis, the Army representative, was succeeded by Maj. C. E. Van Nostrand, who was followed by Col. Oscar Westover and Col. Ira Fravel. Dr. Cottrell succeeded Mr. Orik, and when the former resigned as director of the Bureau of Mines in 1920 he was succeeded by the writer, who had previously been alternate for Dr. Cottrell and remained on the board until October, 1923. He was then succeeded by S. C. Lind, who in turn last year gave place to A. E. Cattell.

Commercial Operations

In an undertaking of the size of the helium project there have been necessarily contributions from a considerable number of people. In an article of this nature it is possible to mention only a few. In some cases the connection was for a short time and in others the influence on the project of an individual lasted for one or two years or even longer. The final result has necessarily been the sum of the constructive contributions of all concerned.

Helium in Natural Gas

The discovery of helium in some natural gas of Kansas by Cady and McFarland in 1907 opened the way for the large developments which have taken place in the last eight years. Up to that time helium was known only in the atmosphere, in gases from certain mineral waters, in minerals, etc., and in none of these sources does it exist in commercial quantities. Apparently, it was destined to remain a rare element with nothing attached to it but scientific interest. Its occurrence in natural gas, however, changed the situation, although it took the war and a considerable amount of imagination and courage to make it possible to utilize it for airships.

The work of Cady and McFarland was an excellent start in determining our helium resources. After we entered the war, however, the Bureau of Mines, in coöperation with the Geological Survey, made a quick survey of our helium natural resources. After the armistice it was decided to continue this survey and the work was carried out under the writer's direction and under the immediate charge of C. W. Seibel. Every gas field in the United States was examined for its helium content and in a number of cases where the percentage of the rare gas was high and the volume of gas also high the field was examined by competent geologists to determine the actual volume of gas available. Most of these results are still held confidential by the Helium Board as necessary to the National Defense and therefore cannot be given in this paper. However, it is permissible to state that, beginning with Texas in the Southwest, the general trend of the helium in natural gas is to the Northeast, going through the Osage in Oklahoma, crossing the southeastern portion of Kansas and going through southeastern Illinois, Indiana, Ohio, Pennsylvania, and New York, and coming back through West Virginia and Kentucky. There is no commercial helium in many of our largest gas fields, such as those of Louisiana, California, Wyoming, etc. There are one or two odd patches in the West which are hard to account for, but the amount of helium-bearing gas there is relatively not great. The following is the analysis of a typical gas:

	Per cent
Helium	0.93
Carbon dioxide	0.25
Oxygen	0.54
Methane	56.85
Ethane and heavier hydrocarbons	10.30
Nitrogen	31.13
	100.00

Table III gives some idea of the large number of gas wells in the United States which contain helium.

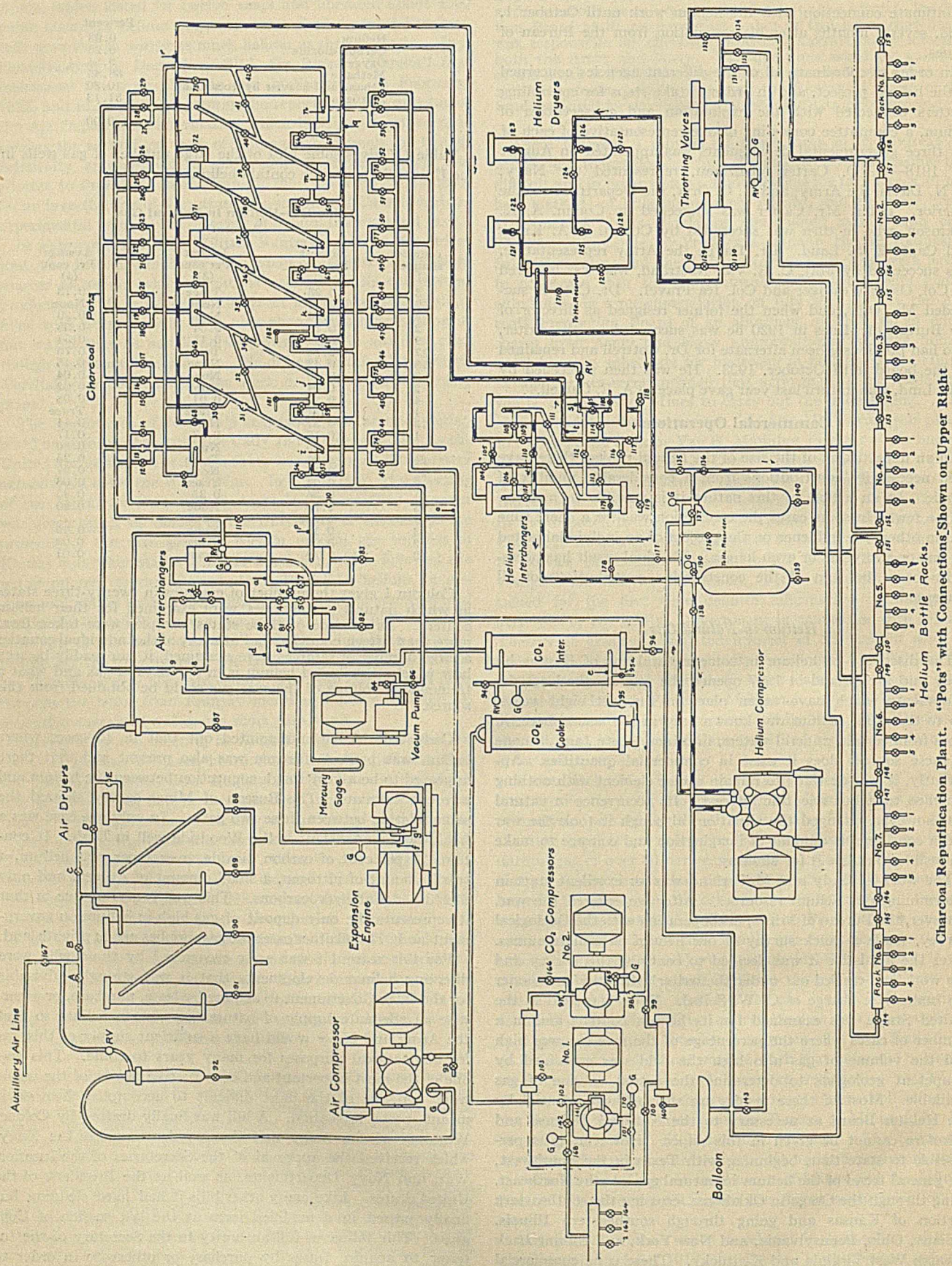
Table III—Helium in Natural Gas
(Per cent)

No. of counties sampled (1)	Highest Per cent (2)	Lowest Per cent (3)	Average Per cent (4)
3	0.26	Trace	0.13
7	0.11	None	None
5	1.04	None	0.20
2	0.12	0.04	0.08
9	0.61	0.11	0.34
17	2.13	Trace	0.76
15	0.43	None	0.15
9	0.19	None	0.04
2	0.04	None	0.02
4	0.27	0.01	0.08
1	Trace	Trace	Trace
13	0.31	None	0.11
1	0.17	0.17	0.17
15	0.55	None	0.30
24	1.04	Trace	0.23
10	0.17	None	0.07
2	0.04	Trace	0.03
1	0.36	0.35	0.35
26	1.73	None	0.43
2	Trace	None	...
3	0.12	None	0.05
2	0.06	Trace	0.03
10	0.10	Trace	0.01

Column 1 gives the number of counties in twenty-three states in which natural gas samples were examined for their helium content. As in some of these states, samples were taken from more than fifteen counties, and in many of the individual counties a large number of samples were examined, it can readily be seen how widely distributed helium is in our natural gas and what a tremendous volume of the rare gas could be obtained from this source.

Cady and McFarland pointed out that in all cases where helium was present nitrogen was also present and that there appeared to be a very rough connection between the helium and nitrogen contents. The Bureau of Mines survey showed the same relation between these two gases. In only one case was a freak gas found. This is the Woodside well in Utah. It contains 27 per cent of carbon dioxide, over 1 per cent helium, a small amount of nitrogen, a small amount of oxygen, and only 2 or 3 per cent hydrocarbons. This well is also unique in that it represents the only deposit of gas high in helium on government land. In all other cases the gas supplies are on private land.

For this reason it was early recognized by those who were directing helium developments that it was strongly advisable for the U. S. Government to acquire by lease, purchase, or otherwise an adequate supply of natural gas rich in helium so that the Army and Navy would have a sufficient supply of this gas for aeronautical purposes for many years to come. This was one of the most important and constructive phases of the whole work and one of the most difficult to accomplish because it meant special legislation. A bill was finally drafted by Colonel Westover of the Army and Commander Kraus of the Navy, which received the approval of the Secretaries of the Interior, War, and Navy Departments, as well as the President of the United States. Like many other bills it had hard sledding but finally passed in a modified form at the last session of Congress. This bill gives full authority to the Secretary of the Interior to acquire leases by purchase or otherwise in order to obtain a reserve of helium-bearing gas for the national defense, but a bill of this character without money does not mean very much and it is now up to Congress to provide the necessary



Charcoal Repurification Plant. "Pots" with Connections Shown on Upper Right Helium Bottle Racks.

funds. It remains to be seen whether Congress will do its full duty. Meanwhile 600 or 700 million cubic feet of helium are going to waste every year in our natural gas, and it becomes increasingly difficult each year to get an adequate supply for reservation without unduly affecting industry or the convenience of local users. Speaking before the Committee on Military Affairs of the House of Representatives in 1924, the writer said: "Every year this matter has been postponed and if Congress does not take action it is going to make it not only harder but more expensive for the American people; therefore, I strongly recommend that this matter be put through at this Congress."

The United States possesses the only large commercial supplies of helium in the world. A relatively small amount exists in the fumaroles of Tuscany, Italy. There is one small gas supply in Ontario, carrying 0.34 per cent helium and one in Alberta, carrying 0.33 per cent. These were the sources used by the Canadians during the war. Quite recently a new supply of helium-bearing gas has been located near Inglewood, Peal County, 35 miles from Toronto, containing about 0.8 per cent helium. The wells are small, so small that they have not been in use for supplying natural gas for ordinary purposes, but it is believed that sufficient helium can be obtained to supply the needs of the University of Toronto for research work. For this reason the Government has purchased the wells for $5000. These supplies of gas are interesting, but for commercial purposes are quite inadequate.

The helium resources of the United States are unique and they have a potential usefulness to this country which is hard to determine at the present time.

Commercial Production of Helium

Before the war most of the helium which existed in the world was obtained by heating radioactive minerals or dissolving them in acid. The total amount in existence was probably not more than 10 or 12 cubic feet. Therefore, the sudden determination to produce the rare gas in quantities sufficient for airships meant the starting of an entirely new and difficult technical project. We at once decided that probably the most efficient method was that of refrigeration. Fortunately, we had two commercial organizations, each possessing a trained technical force that was immediately available. The coöperation of the Linde Air Products Company and the Air Reduction Sales Company was invoked and these organizations operated their own plants under the general control of the Government.

Following the operations of the small experimental plants during the War, which have already been described,[11] it was decided to build a large production plant at Fort Worth, using the Linde system.

In order to get its cooling effect the Linde Company uses nozzle expansion of the gas, getting thereby the Joule Thomson effect. This method is not so efficient as adiabatic expansion in an expansion engine except near the critical temperature of the gas, when the nozzle becomes nearly as efficient as the expansion engine.

In the production plant as first designed by the Linde Company the natural gas is treated for the removal of carbon dioxide, which is present in quantities varying from 0.2 to 0.3 per cent. This is done by bringing the gas under low pressure in contact with limewater in specially designed scrubbers. The natural gas free from carbon dioxide passes under low pressure to two gas-holders, which act as reservoirs for the compressors. The heat of compression is removed in the usual way through intercoolers between each stage of compression and after-coolers in which the gas is cooled by circulating water. In addition to obtaining refrigeration by nozzle expansion a carbon dioxide cycle is also used as a gas fore-cooler. The compressed gas is led through this fore-cooler, in which most of the water vapor is removed by freezing. The cooled gas goes from the fore-cooler to the gas interchangers, where it meets the cold gas returning from the still. This returning gas pre-cools the incoming gas to a temperature sufficiently low to give the desired effect after expansion. Arrangements are made in connection with these interchangers so that there is a progressive cooling first carried out by the returning vapors of the heavy hydrocarbons and ending up with the returning nitrogen which is liquefied in the upper portion of the still. From the interchangers the gas is expanded through a nozzle into the still and enters the bottom of the still partly in the liquid and partly in the gaseous state. The still consists of three units, each unit being a rectification column with a condenser at the top and a receiver at the lower end. The gas enters the lower unit and passes up through the middle unit and thence to the top unit. Each of these units is so designed as to remove a definite portion of the constituents of the gas in the liquid state and deliver a definite portion of the gas in the gaseous state to the next higher unit. A definite temperature gradient is maintained in each unit and the constituents are progressively removed by liquefaction and reëvaporation and go back through the interchangers. In order to get a reasonably high-grade product containing as much as 70 per cent helium, it is necessary to liquefy the nitrogen in the gas as completely as possible. In order to do this and not have the vapor pressure of the nitrogen too high the upper portion of the still should be near the temperature of liquid nitrogen. In order to accomplish this a separate nitrogen cycle has been used in which nitrogen is liquefied and surrounds the condensers of the upper unit of the still. The make-up for this nitrogen cycle in the original experimental plant was purchased, but the production plant was designed to obtain the necessary nitrogen from the natural gas in the operation of the plant itself, the nitrogen being obtained by the final fractionation of nitrogen from the methane in the upper portion of the still. Actually, the purity of this nitrogen has not been so high as expected, but this fact has not seriously affected the operations of the plant.

The liquids collected in the receivers of each unit are used as required in the condensers of the middle and lower units. All outgoing gases from the still pass through the gas interchangers and gas fore-coolers, thus pre-cooling the incoming natural gas. These outgoing gases are mixed at the final outlet and are returned to the mains which supply the cities of Dallas and Fort Worth. The gas, therefore, is simply robbed of its helium and a small portion of nitrogen, the rest of the gas being used for commercial heating and lighting purposes.

The cost of helium per thousand cubic feet in the small experimental plant during and immediately after the war varied from $300 to $400. This cost was considerably reduced after the production plant was in steady operation, but even in the fall of 1922 it was as high as $120 per thousand cubic feet without allowing for amortization of plant equipment or interest on investment. The plant operated smoothly and steadily, but recoveries were not good, and the whole question of recovering helium from natural gas was so different from the separation of oxygen from nitrogen that there was no question about the fact that not only small improvements but radical improvements were possible. The Jeffries-Norton Plant at Petrolia employed the idea of fractional liquefaction more definitely than was involved in the other processes used, and the writer very early became convinced that a careful laboratory study of the exact conditions under which the various components were liquefied from natural gas would lead to results of considerable importance. Such a line of work would give reasonably quick information and then a more careful study of the solubility of helium under definite conditions in the various liquid hydrocarbons which compose natural gas, a study of vapor pressures at various temperatures, as well as the specific heats, of these hydrocarbons, and work of a similar nature would give additional information

[11] Moore, *J. Franklin Inst.* **191**, 145 (1921).

that would be of value in the designing of a new process or the improving of those already in existence.

With this object in mind the writer obtained from the Army and Navy the necessary funds for the establishment of the Cryogenic Laboratory, and this laboratory is still operating. Work on solubilities, fractional liquefaction, etc., was carried out and gave valuable information that has been used in the designing and improvement of processes. It is unfortunate that details cannot be given owing to the fact that the Government is not yet ready to release them.

While the work just described promises to assist materially in the reduction of the cost of helium, the production figures have been steadily reduced at the government plant at Fort Worth, which until last summer was operated under the supervision of the Navy by engineers loaned by the Linde Company, but is now under the Bureau of Mines. The average grade of the gas shipped has been 93 per cent and the cost of producing this per thousand cubic feet has gradually fallen since the middle of 1924 at which time the plant expense per thousand was $80. During the summer and fall of 1925, for several months it has been as low as $30 per thousand. Lately the variations have been mainly due to a lack of adequate gas supply. The Petrolia gas field is "on its last legs" and is only being kept up by continually drilling and the bringing in of fresh wells, which, however, have only a short life. Unless Congress acts and acts quickly in the way of supplying sufficient funds for acquiring a new supply of gas, it will be found more and more difficult to obtain the quantity required to run the plant at full capacity. Fortunately, such a gas supply is available at no great distance and there will be no possible excuse for not taking care of the situation. As long as the plant is run at full capacity it can produce from 1,000,000 to 1,200,000 cubic feet of helium per month at an operating cost of $30 per thousand cubic feet or even lower. If the gas supply is reduced to 600,000 cubic feet per month the operating cost will go close to $40 per thousand.

There is plenty of helium, provided it is made available to the necessary production plants. It has been observed that one gas field high in helium contains nearly 100 billion cubic feet of natural gas. This would furnish 2 million cubic feet of helium per month for a period of from twelve to fifteen years. Such a supply of helium would keep five airships of the size of the Los Angeles constantly in operation after they were once filled. Another gas field contains probably twice the volume of gas that is in the one described above, and although the helium content is not so large, the total volume of helium available is probably greater.

During the last year and a half some decided improvements have been made in the Fort Worth plant. This plant was originally designed by the Linde company to take the high-pressure gas from the pipe line and reduce it to atmospheric pressure so as to use the Linde method of removing carbon dioxide by means of milk of lime at low pressure. The gas was then recompressed and sent to the liquefaction system. The Jeffries-Norton process took the gas from the pipe line at pipe-line pressure and, whereas this plant was not originally designed for the removal of carbon dioxide, the writer early realized that such removal was necessary and had installed at Petrolia high-pressure purifiers using caustic soda for the removal of carbon dioxide. This was also done at Fort Worth last year, although the method used was a novel one designed by the Navy engineers in charge, in which the caustic soda solution was actually introduced into the pipe line along with the gas. In order to recover the sodium carbonate a recausticizing plant has been installed, which will reduce considerably the total cost of the removal of carbon dioxide. In addition, in order to improve the total recovery of helium, the average grade of the gas formed in the first step of the process has been reduced from 65 or 70 per cent down to 50 per cent, or even lower. In other words, the higher the grade of gas produced in the first step the lower is the recovery. It has also been possible to do away with the auxiliary nitrogen refrigeration cycle. All these changes have resulted in a material reduction in the cost of helium, as already indicated.

Repurification

Any gas used in an airship diffuses from the bags. Therefore, there is a steady actual loss of gas and, in addition, the gas remaining in the bags gradually decreases in purity. It is the practice when hydrogen is used to valve a certain amount periodically whether the airship is flown or not, and this valved gas is replaced by fresh hydrogen. In this manner the purity of the gas is kept above a certain point. With helium, valving is only resorted to when absolutely necessary. This practice is necessary more on account of the limited capacity of the one plant available than to the actual cost of the gas itself. Therefore, the purity of the helium gradually drops and the lifting power also drops. At a certain point, therefore, usually when the gas is about 85 per cent pure, the helium is pumped out and "repurified," which simply means taking the air out, raising the purity, and using the helium over again. Since the cost of purification is very much less than the initial cost of production, the more often a gas is purified and reused, the lower its relative total cost becomes compared with hydrogen, because the latter is never repurified and is always discarded. Therefore, this whole question of repurification is an important one and has received a good deal of attention from the Bureau of Mines.

The Army Air Service was the first to realize fully in a practical manner this phase of the helium project. They started the construction of a plant at Langley Field with H. N. Davis as consultant. Owing to various difficulties before it was completed they asked the Bureau of Mines to take it over and finish it.

This was done, but owing to an accident in the plant and also to a change of base for Army airships it was never run on a production basis. Another small repurification plant on two railroad cars was also started by the Army Air Service. The object of this was to have a small plant which could go to a disabled airship when the airship could not come to the plant. Before this was completed it was also turned over to the Bureau of Mines and was adapted for the use of charcoal at low temperatures as a purifying agent. When the Shenandoah was nearly completed the Navy requested the Bureau of Mines to design a repurification plant for the Lakehurst Station based on the general principles of the Langley Field plant, using high pressure and low temperature for the separation of air from helium. This was done and has been in successful operation ever since, constantly repurifying the gas used in the Shenandoah and Los Angeles.

Repurification by Means of Charcoal—At the time the railroad cars were taken over from the Army for completion by the Bureau of Mines it had not been definitely decided what system of refrigeration and purification would be used. A complete power unit had been installed in one of the cars and two compressors were available in the other. At this time the operating end of the Army Air Service was becoming exercised over the lifting power of the helium they would have to use. One hundred per cent helium has 92 per cent of the lifting power of 100 per cent hydrogen, but the plant at Fort Worth was then supplying helium of 91 or 92 per cent and this had a very different lifting power than relatively pure hydrogen. The Shenandoah had been built for hydrogen and the use of helium, even if pure, would mean that the range of operation of the airship would be decreased because it would not be able to carry so much gasoline.

Operating with 92 per cent helium meant a further reduction in this range of operation. It therefore became important for the technical men to supply a gas of much higher grade than

92 per cent. Preliminary experimental work in the Cryogenic Laboratory showed that if activated charcoal was used at low temperatures it completely adsorbed all the impurities from the helium and gave a gas of practically 100 per cent purity. Not only was this true but as the impurities were adsorbed the purity of the helium remained constant until the saturation point of charcoal for air was reached, and then the break in the purity was very sharp and was immediately registered by automatic recorders. Figure 1 shows the sharp break in purity when saturation is reached—40-minute chloropicrin charcoal was used in this experiment. Fifty-five-minute charcoal gave a 30 per cent improved result.

This work, which was carried out by C. W. Seibel and Leo Finkelstein, led to the use of charcoal in the small railroad plant.

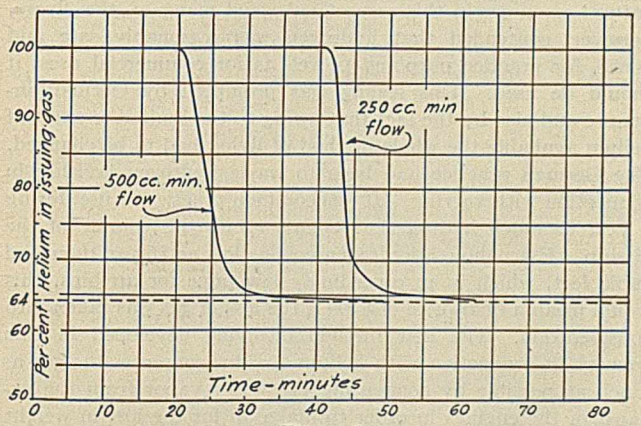


Figure 1

The refrigeration was obtained by means of an air compressor operating with a Claude type expansion engine and interchangers. The refrigerated air was used for cooling the charcoal in six charcoal "pots" each containing 40 pounds of activated charcoal. Whereas the adsorption naturally increased with the lowering of the temperature, it was found that the increased efficiency below −120° C. was not sufficient to justify going below that temperature and reasonably satisfactory results were obtained at −100° C. The construction of the charcoal "pots" was somewhat similar to that of a tubular boiler, the air entering at one end and passing up through the tubes, whereas the granular charcoal was tightly packed in between the tubes. While one "pot" was actually adsorbing one was being "out-gassed" or warmed up for the elimination of the air adsorbed by the charcoal, and others were being progressively cooled down for use when the charcoal in the "pot" actually in service became saturated. The pressure on the helium cycle was only what was necessary to drive the gas through the charcoal—a few pounds. A carbon dioxide cycle was also installed in order to have some additional refrigeration if needed. With an adequate supply of air compressed to 600 pounds pressure, the plant was capable of purifying approximately 500 cubic feet of 80 per cent helium per hour, stepping the purity up to 99+ per cent. The plant was too complicated for successful operation on such a small scale, however, as the number of valves to be changed was large and required the constant attention of the operators. In addition, at the time the plant was designed helium was costing at Fort Worth about $120 per thousand cubic feet and therefore it was then practical to have a repurification plant in which the costs were as high as $20 to $30 per thousand. The more recent success of the Lakehurst plant has indicated so plainly that a sufficiently high purity can be obtained without the use of charcoal that it has been abandoned as a repurification medium. The railroad plant is now being modified for repurification purposes along the general line of the Lakehurst plant.

Lakehurst Repurification Plant—When the low-grade helium at Fort Worth was "stepped" up to 91 or 92 per cent it was done at a pressure of 1000 pounds on the cycle. Therefore, when the Lakehurst plant was designed by the Bureau of Mines for the Navy on account of the necessity for high-grade helium already mentioned, it was decided to use 1800 pounds pressure on the helium cycle. This theoretically gave at the temperature of liquid air a purity of about 99 per cent helium, and the actual purity obtained has averaged 98 per cent. The principle used is the simple one of pumping helium under high pressure through a coil or purifier to which is attached a "drain pot" for the liquefied impurities (air), the whole dipping in a bath of liquid air which is obtained by means of a separate cycle. All condensed liquids are reëvaporated to pre-cool the incoming gases and the refrigeration contained in the purified helium is also used to pre-cool the incoming helium. The air cycle is the regular Claude system. After being compressed to 600 pounds the air goes through the drying and carbon dioxide removal apparatus and then through a Claude interchanger, after which it divides, about 25 per cent going through the liquefier and 75 per cent through the expansion engine in the usual way. The liquid air and cooled gases are used for cooling the coils and "purge pot" in the purifier. The impure helium is compressed, as already stated, to 1800 pounds, and after being dried goes through its own interchanger into the purifier.

This plant was designed to "step up" helium from 80 per cent to 98 per cent, but it has successfully run continuously on helium of purity as low as 48 per cent at the rate of 20,000 cubic feet of impure gas per hour. It has been exceedingly successful and efficient. Owing to the fact that operations necessarily have to be intermittent, the repurifying costs are much higher than if the operations could be continuous. However, if the technical force can be used on other work between periods of operation the cost of repurification is exceedingly low, about $2 or $3 per thousand cubic feet. C. W. Seibel and C. F. Cook are largely responsible for the success of this plant.

Airships

It is not possible in an article of this kind to do more than merely touch on the development and future use of airships. Up to the war all such developments were carried on in Germany; during the war England, France, and Italy got into the game; since the war, most of the development connected with rigid airships has been carried on in this country. Indeed, it is probable that had it not been for the construction of the Shenandoah there would have been little or no progress in any country in lighter-than-air ships for perhaps a decade.

At the present time England has two large rigids under construction for use between England and the Far East. These have a capacity of 5,000,000 cubic feet, or twice that of the Los Angeles, with a length of 830 feet and a maximum diameter of 110 feet. It is expected that these giants of the air will reach lower Egypt in two days and Australia in 10 days. Since the British do not possess any adequate supply of helium, these vessels will be filled with hydrogen and will be able to carry over 40 tons of useful load with an operating range of 3000 miles fully loaded. In war times by carrying more fuel it would be possible for them to have a range of action of more than 15,000 miles. When the "useful" lift is taken into consideration (the lift in addition to the weight of the airship itself), the foregoing figures for hydrogen would have to be reduced between 20 and 25 per cent for helium. It is expected that these airships will carry one hundred and twenty people.

It can be readily seen from these figures what the possibilities are. The operations of the Los Angeles and the Shenandoah have given a practical demonstration of the airworthiness of airships to a great number of American people. Unfortunately, some advocates of the airplane feel that it is necessary to "knock" the airship in order to boost the airplane on the basis that whatever money is not spent on "lighter-than-air" will be spent on

"heavier-than-air." The tragedy of the Shenandoah has given these opponents of the airship a good talking point, and yet the real value of the airship should be determined by what it has done under known conditions and not by what it has not done under rather uncertain conditions. The Shenandoah tore loose from its mooring mast at Lakehurst in a storm and was brought back to its hangar safely although in a badly disabled condition. A British airship repeated a similar performance under almost identical conditions, with the same results, in weather that prevented all commercial airplanes in the British Isles from taking the air.

The construction of the Shenandoah was not perfect, but was thoroughly up to date at the time she was built. Perhaps the greatest weakness in her design was the fact that she was not specially constructed to withstand a torsional strain. According to Col. E. C. Hall, of the Army Air Service, who was on the Shenandoah when it was wrecked, this is exactly what the airship had to withstand. In talking to the writer he said that as he looked out of the window of the cabin towards the tail of the ship just before the break he could see that the airship was in a "twister" and was being subjected to a decided torsional strain. In his opinion that was what caused the wreck. In the later design of the Los Angeles allowances have been made for this kind of a strain and it is possible that the Los Angeles for this reason might have withstood what was fatal to the Shenandoah. We learn by experience. And yet critics of the airship do not expect a house, a barn, an automobile, or even a train to withstand a cyclone and certainly do not advocate that we stop building these useful commodities. The Shenandoah struck a cyclone between two storms, which did not, however, reach the earth and, therefore, was not felt severely on the land. Weather officials have considered it safe to travel between two storm areas; they now know that this cannot always be done and in future both airplanes and airships will go around, instead of between. No airplane could have existed for a moment where the Shenandoah was wrecked, according to Colonel Hall, and yet the airship in development is about where the airplane was ten years ago.

There need be no conflict between the two, as each has its own distinct use with only a small amount of overlapping. At the present time plans are being formulated for the development of commercial airships in this country and the writer expects to be able to travel under such conditions within two or three years, if not before.

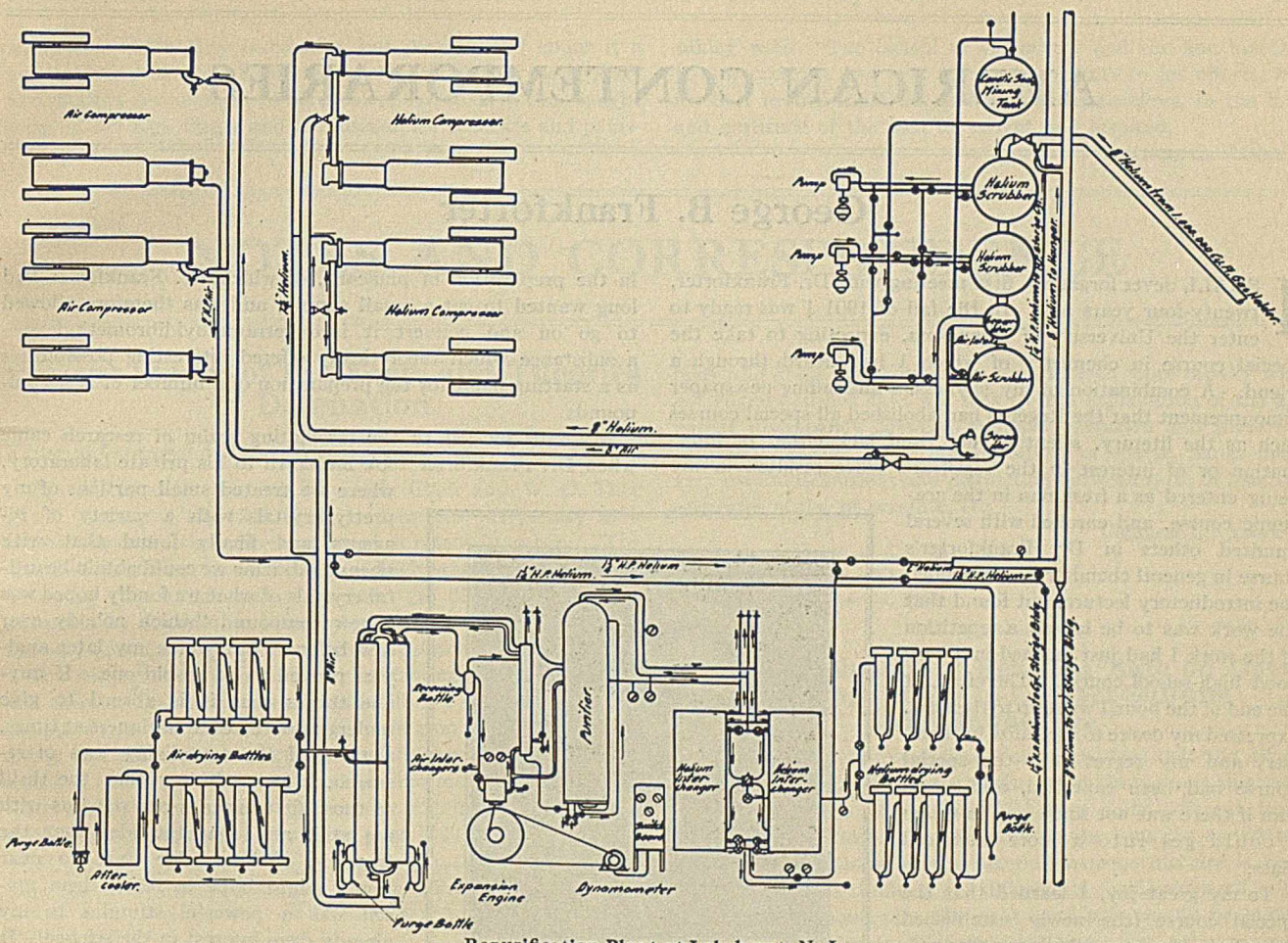
There are many improvements which can still be made in airships and these improvements will add to the speed, safety, and general efficiency of this method of travel. A more detailed study of the strains that such ships have to withstand under difficult conditions is required. At present the factor of safety has to be reduced as much as possible in order to take care of as great a lifting power as possible, and therefore a better knowledge of just what the airship has to withstand is required. Definite improvements in structural alloys are needed. Duralumin is fairly satisfactory, but as it is necessary for it to be heat-treated there is always a possibility of certain portions of the framework not being quite so good as others. In addition, this alloy is subject to deterioration so that the original strength is not always maintained. Improvements in alloys of this character giving both additional strength and permanency are greatly to be desired.

A substitute for goldbeater's skins in the making of the gas bags is also needed. If a rubberized fabric can be produced that will not require any additional weight in the bags and at the same time will make them as impervious to the diffusion of gases as is the case with goldbeaters' skin, a decided step forward will be achieved. Improved engines using heavy oil instead of gasoline, better water vapor condensers, more efficient methods of hanging the passenger cars, gondolas, etc., to the main framework, represent some of the important steps that are necessary. These will all undoubtedly be achieved in the near future and will add to the general efficiency of the airship. A recent design by the Goodyear Company of a 6,000,000 cubic foot ship takes care of some of them.

Use of Helium in Airships

For some time there was a considerable difference of opinion among men who operated airships in this country as to the wisdom of using helium on all occasions for flying purposes. Practically every one admitted its great advantage in war times, and every one agreed that methods for the commercial production of helium should be perfected so that if the United States ever went to war we would be able to take advantage of our natural resources in this respect. A good many of the flyers, however, contended that hydrogen was reasonably safe and hence, for practice purposes as well as for commercial uses, it should be used. This feeling was prompted by German influence and also by the fact that owing to the limited amount of helium available the whole method of flying had to be changed. The German practice had been to waste hydrogen lavishly in connection with valving. It was common practice to use during a year as much hydrogen as twenty times the volume of the airship. Even though hydrogen cost as low as $5 per thousand cubic feet, which is an exceedingly low price for airships, this would mean a final price of $100 if the loss of gas was taken into consideration. The new method of flying developed in this country in connection with helium airships conserves the gas as much as possible by condensing the water vapor from the exhaust of the engines in order to make up for the loss in weight of the gasoline consumed. Then by driving the ship down by means of her engines whenever possible, instead of valving, it is practicable to fly an airship containing helium more or less continuously with a gas "make-up" of not more than 200 per cent per annum. With helium at $30 to $40 a thousand cubic feet, this represents a lower "make-up" cost than with hydrogen at $5 a thousand. In addition, as already stated, helium is repurified and used over again, which cuts the total cost at least 25 per cent, if not more. The figure of $30 to $40 for helium is conservative for what the gas should cost within a year or two, including all overhead, amortization, transportation, etc. An ex-German airship captain, who is in this country and has received a great deal more advertisement than has been justified, has made numerous misstatements concerning helium and its use in airships. In a recent article in a well-known magazine he says that the quantity available for airships is extremely small and that the gas is found only in a few wells in Texas. The early part of this article shows conclusively that both of those statements are untrue. This same writer belittles the fire hazard in connection with the use of hydrogen. It is quite true that a man who is daily subjected to a risk becomes inured to that risk to such an extent that the danger becomes minimized in his mind. This, however, does not change the danger itself. Every airship disaster during the last few years has resulted in the burning of the ship, with the exception of the Shenandoah, which was filled with helium. Most of the German ships destroyed before and during the war had the same experience. Fire either started the disaster or was an accompaniment of it. People who talk glibly about the absolute safety of a hydrogen-filled airship are either stupid or have an ulterior motive either financial or something worse. This country has in its helium resources a natural advantage that should not be given up for one moment in exchange for interested and prejudiced talk.

The men who are looking forward to commercial aviation in this country and who are working to this end recognize fully the fact that helium must be used. In the magazine *U. S. Air Service*, under date of February, 1922, Commander Lansdowne wrote, after testing out helium in the Navy Blimp C-7, as follows:



Repurification Plant at Lakehurst, N. J.

Air cycle on the left, helium cycle on the right. Compressors for both cycles on upper left and scrubbers for both cycles on upper right.

The actual use of helium in an airship exceeds all the calculations of an expert in its performance. In fifteen flights from December 1 to 15 not one particle of gas was lost from the airship. The original amount that went into the bags on December 1 was not added to or reduced by valving or diffusion or replacement. Such performance could not be duplicated by hydrogen. The other features in connection with the use of helium make it the *one* gas for balloons and airships.

The present attitude of the Army and Navy flyers is fairly definite notwithstanding the early difference of opinion. They are for helium, provided they are given sufficient gas to fly their ships—they do not wish them kept in the hangar through a lack of sufficient gas supply. Up to the present the plant at Fort Worth has produced more than 25,000,000 cubic feet of the rare gas. Of this, 20,000,000 cubic feet have been produced since September 30, 1923, and owing to a loss from storage due to leaky valves, etc., this total amount has not actually been available. In addition, a considerable amount of gas was lost before the Shenandoah was under the command of Lansdowne, owing to the German methods of flying. There has not been, therefore, sufficient gas for both the Shenandoah and the Los Angeles at the same time. The answer is simply additional plant capacity, to be provided for by Congress. The gas is available for fifty ships, if necessary, but the present plant cannot produce more than 12 to 14 million cubic feet of gas a year, even when the gas supply is adequate, and as only half of this gas goes to the Navy it can readily be seen that this amount is not sufficient to keep two ships in the air most of the time. This is not the fault of helium. It is a matter to be brought to the attention of Congress with sufficient pressure behind it from the country to make Congress act.

Shortly after the disaster to the Shenandoah the writer sat at a table in the dining-room of a New York hotel opposite Col. E. C. Hall, of the Army Air Service, one of the survivors of the Shenandoah disaster. As he described his experience his face was serious, as undoubtedly he was thinking of the gallant comrades who had been lost on the occasion in question.

"If the control car had been attached in a different way to the framework and had not broken away, only three or four men out of the total crew would have been lost," he said.

"What did you say when you and the other survivors got on terra firma," he was asked.

"What did we say," he replied, "why we turned to each other and said 'thank God for helium'."

Armour Institute of Technology Merges with Northwestern University

Formal steps toward the merger of Armour Institute of Technology with Northwestern University were taken on January 9, 1926, when the trustees of the two institutions signed contracts detailing the affiliation plan.

The plan includes the raising of a $10,000,000 endowment fund; erection on Northwestern University's Evanston campus of ten new dormitories for men at an estimated cost of $80,000 each; expansion to three times its size of the Swift hall of engineering at Northwestern; construction of one addition to machinery hall; construction of two new science buildings; and the erection of one machinery hall on Northwestern's downtown campus to accommodate between 800 to 1000 part-time students.

The new engineering school will be known as the Armour College of Engineering of Northwestern University. The retention of the Armour name is in memory of Philip D. Armour, whose initial contribution of $1,000,000 in 1893 founded the Armour Institute. The Chicago Art Institute will continue to house the Armour School of Architecture.

AMERICAN CONTEMPORARIES

George B. Frankforter

I SHALL never forget my first meeting with Dr. Frankforter, twenty-four years ago. In the fall of 1901 I was ready to enter the University of Minnesota, expecting to take the special course in chemistry of which I had heard through a friend. A combination of my shyness, a misleading newspaper announcement that the Regents had abolished all special courses such as the literary, scientific, etc., and lack either of information or of interest in the registrar's office resulted in my being entered as a freshman in the academic course, and enrolled with several hundred others in Dr. Frankforter's course in general chemistry. I attended the introductory lecture, but found that the work was to be largely a repetition of the work I had just finished in a very good high-school course. Therefore, at the end of the hour I went up to the desk, expressed my desire to specialize in chemistry and my regret that the special course had been cancelled, and asked him if there was not some way in which I could get into a more advanced class.

George B. Frankforter

To my great joy, I learned that the special course (the newly established School of Chemistry, which was the apple of his eye) emphatically had not been abolished, and that my registration could be changed. A note from him to the Registrar resulted in the desired shift, so I started in at once on qualitative analysis and missed the rest of the general chemistry lectures. I have always regretted that I did not manage to hear them later; he was considered (and rightly I believe) in those days to be one of the best and most interesting lecturers on the campus, and his polished presentation, apt experiments, and courtly bow at the close of each lecture were famous among the students.

A year of hard work brought me again to him—this time to hear his lectures in organic chemistry. If general chemistry was the "show course," organic was the one that was closest to his heart. He scorned notes, and the enthusiastic and logical presentation of the interesting intricacies of the compounds of carbon, and the kaleidoscopic changes which they could undergo in organic syntheses, made an impression upon my mind which the years have been unable to erase, and which rendered the study of the text almost superfluous, so vivid and clear was the mental picture.

He had a rare ability of infecting the class with his own enthusiasm and love of the subject, and most of us spent at least twice as much time as was required in the laboratory, so that I remember there was some complaint about the disproportionately large cost for chemicals and glassware in that course in comparison to the moderate fixed fee which we paid for it.

When we had finished the required work we were introduced to chemical literature, by being assigned the work of the original discoverer of some compound to look up in the library, and were then allowed to try to follow his directions and prepare the compound. I was fortunate enough to have good luck in the preparation of pinacone, of which Dr. Frankforter had long wanted to get a small supply, and was therefore allowed to go on and convert it into tetramethyldibromethylene—a substance which theoretically offered interesting possibilities as a starting point for the preparation of a number of new compounds.

My introduction to the fascinating realm of research came when Dr. Frankforter took me down to his private laboratory, where we treated small portions of my pretty crystals with a variety of reagents, and finally found that with phenylhydrazine we could obtain beautiful crystals of what we fondly hoped was a new compound "which nobody ever saw before," but which my later analyses proved to be an old one. If anyone thinks that it is absurd to give undergraduates, even beginners at times, a taste of the tantalizing joys of research, I can only say that the thrill of those first experiments remains with me still, and that the idea that the frontiers of knowledge were so near that I might hope to reach them myself was a powerful stimulus to my already deep interest in the science. It seems to require the personal touch of a great teacher, in most cases at least, to pass on to the student the fiery zeal of the true research spirit, and I have never known a teacher who could do this better than he.

Unfortunately, the pressing demands made on his time, not only by a heavy teaching schedule but also by deans' meetings, faculty and committee meetings, and the routine executive work involved in the management of a large chemical laboratory with an inadequate and overburdened faculty, gave him so little time for research that very few students had a chance to work with him, and the little time he was able to give them was often only obtained by locking the office door and failing to hear the knocks of callers. This, of course, involved a continual pressure of university work waiting to be done, in spite of the use of most evenings and holidays, and many Sundays. It is a sad commentary on university organization here that so many of the best teachers have so little time to teach, on account of the pressure of college business and routine administrative work that could just as well be done by others. It was not until he returned from his service in the Army and with the War Claims Board after the late war that he was relieved of this burden and given an opportunity to work and teach for a few years at least in comparative leisure.

This year he has rounded out thirty-five years of service as professor of chemistry at the University of Minnesota. He has seen the number of undergraduates taking chemistry grow from a hundred or so to several thousand; and from the School of Chemistry, for which he struggled so long and endured so much, a steady though small stream of well-trained graduates have gone to make names and places for themselves in the chemical field. Many of them saw little of him and failed to under-

stand how much they owed him, but personally I count it a great privilege to have been associated with him for many years as a student and member of his faculty, and to have thus caught some of his high ideals and enthusiasm for accurate and painstaking work. The School of Chemistry and the fine building it now occupies are, in a sense, monuments to his efforts, but his best reward must lie, as for all great teachers, in the love and gratitude of the men he taught and inspired.

FRANCIS C. FRARY

NOTES AND CORRESPONDENCE

Present Status of the Facts and Theories of Detonation

Editor of Industrial and Engineering Chemistry:

The article under this title by G. L. Clark and W. C. Thee [THIS JOURNAL, 17, 1219 (1925)] interested me greatly as a critical review of the subject as found in recent literature. The recent work of Bone on combustion at high pressures, the original theory of "detonation control by inert gas diluent," originally advanced by Ricardo, and the later work of Alcock are about the only recent important phases not mentioned.

This subject is so complicated by conflicting, unclassified facts and theories that it is an extremely difficult subject to review adequately in one paper without "treading on some one's toes," unless the conflicting evidence is first further coördinated and classified. Among some of the assertions made by Clark and Thee with which I cannot agree is the statement found in the second paragraph, second column on page 1223:

> Woodbury, Lewis, and Canby, firing acetylene-air mixtures, state that increased temperature produced little effect upon the rate of flame propagation. With this Brown, Leslie, and Hunn seem to agree.

The paper "Gaseous Explosions. I—Initial Temperature and Rate of Rise of Pressure" [THIS JOURNAL, 17, 397 (1925)] presented complete experimental and theoretical evidence that initial temperature (not ignition temperature) has a pronounced effect upon the rate of rise of pressure, flame propagation, and detonation in all homogeneous reactions. I cannot understand how any one could read this paper, the abstract, or even its title, and conclude that we believe "increased temperature produced little effect upon the rate of flame propagation."

GEO. GRANGER BROWN

UNIVERSITY OF MICHIGAN
ANN ARBOR, MICH.
December 12, 1925

. . . . . .

Editor of Industrial and Engineering Chemistry:

The writers of the paper on the "Present Status of the Facts and Theories of Detonation" greatly regret that the first two sentences of the second paragraph, second column, page 1223, have suffered in the process of condensation of the paper, and lead to a mistaken interpretation of the work of Woodbury, Lewis, and Canby, and of Brown, Leslie, and Hunn.

The word "such" should be inserted before "effect" in the first sentence, in order to refer back to the assertion by Mallard in the preceding sentence that increase in initial temperature increases speed of propagation, rate of combustion, rate of rise of pressure, etc. Following the word propagation should be inserted, "but that increases in temperature above a certain definite value are actually accompanied by a decrease in the rate of combustion." These omissions were overlooked in the final form of the paper, probably because of confusion between ignition temperature and initial temperature. We shall appreciate publication of these corrections.

In the opinion of the writers, however, the drivers of automobiles who know that detonation occurs much more rapidly with hot engines on hot days will seek to find explanation of the apparent discrepancy between practical operation and these experimental results. The interpretation, of course, hangs upon very careful definitions and distinction between rates of reaction and rates of rise of pressure, etc.

GEORGE L. CLARK

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASS.
December 29, 1925

Note on "Influence of Reaction Rate on Operating Conditions in Contact Sulfuric Acid Manufacture"

The authors wish to call attention to the fact that the differential equation for reaction rate employed throughout this article [THIS JOURNAL, 17, 593 (1925)] is in units different from those ordinarily used. Furthermore, in the equation as written the change in volume of the reacting gaseous mixture is neglected in so far as it affects the differential coefficient itself. To make the equation exact the right-hand side should be multiplied by the volume. The reaction constants as computed, while proportional to the constants expressed in absolute units, are also functions of the total pressure and temperature. For constant pressure conversion the equations given need no modification unless the pressure is other than atmospheric or the change in total mols of the reacting mixture is considerable.

W. K. LEWIS
E. D. RIES

Preparation of an Ash-Free Wood Charcoal

In the recent note by the author, THIS JOURNAL, 17, 1114 (1925), he unintentionally neglected to mention that Max Latshaw first prepared the charcoal under the author's direction. This method became routine in the author's laboratory when wood charcoal was needed, and as such the note was written.

L. H. REYERSON

Calendar of Meetings

American Ceramic Society—Atlanta, Ga., February 8 to 13, 1926.

American Chemical Society—71st Meeting, Tulsa, Okla., April 5 to 9, 1926.

American Electrochemical Society—Chicago Beach Hotel, Chicago, Ill., April 22 to 24, 1926.

Association of Chemical Equipment Manufacturers—2nd Chemical Equipment Exposition, Cleveland, Ohio, May 10 to 15, 1926.

American Institute of Chemical Engineers—Berlin, N. H., June 21 to 23, 1926.

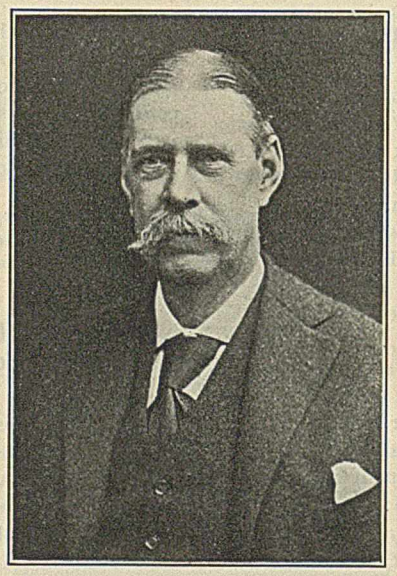
Fourth Annual Colloid Symposium—Massachusetts Institute of Technology, Cambridge, Mass., June 23 to 25, 1926.

The diagram of the apparatus accompanying the article entitled "Use of Methyl Salicylate in a Flowmeter," by R. H. K. Foster, THIS JOURNAL, 18, 82 (1926), should be inverted.

Charles Avery Doremus

FOLLOWING the services at St. Thomas' Church for Prof. Charles F. Chandler, I walked down Fifth Avenue with Dr. Doremus. "I am getting along pretty well myself," he remarked. But it came almost as a shock to learn that he was seventy-four.

Those who attended the College of the City of New York in the old days of stern military discipline under General Alexander S. Webb, a hero of Gettysburg, when the motto was "Make good, or make way," and a class starting with eight hundred would graduate about eighty, will never forget their induction into physical and chemical science by Prof. Robert Ogden Doremus and his assistants, Professors Charles Avery Doremus (his son) and L. Heinrich Friedburg.



Charles Avery Doremus

Prof. R. Ogden Doremus had done splendid work in popularizing science, and his forceful lectures were reënforced by a host of stories drawn from his extensive experience. His "Write, you sinners! Write!" and stories about Ole Bull, Professor Draper, and "my former assistant Dr. Wilkinson," are remembered by many until this day; and despite the lack of one forearm, he was a skilled experimenter, a good amateur painter, and an accomplished musician. Occasionally, "my son" gave the lecture on the rare occasions when "father" was absent; and later with Dr. Friedburg, "Charley" introduced us into the mysteries of qualitative and quantitative analysis. It is hard to realize that the tall, handsome, bearded gentleman of those days has passed on.

Following his graduation from the College of the City of New York, in 1870, he went to Heidelberg to take his Ph.D., and the story is told that one of the professors there on seeing this six-footer burst out—"Was für ein Bübschen ist dass!"—not realizing, perhaps, that he would be understood. "Ich bin das Bübschen des Professor Doremus," smilingly replied "Charley."

Soon after his return here, he became assistant in chemistry, toxicology, and medical jurisprudence at Bellevue Medical College; and besides his Alma Mater, Buffalo Medical College, and the American Veterinary College claimed his services. He was one of the few surviving charter members of the AMERICAN CHEMICAL SOCIETY, and in the "middle ages" when the New York Section used to meet in Professor Doremus' lecture room at 23rd Street and Lexington Avenue, he rendered yeoman's service in getting new members and creating enthusiasm. He also became a leading light in the American Electrochemical Society, and was a member of the Association for the Advancement of Science, the Society of Chemical Industry, and associate member of the Society of Electrical Engineers, the Medico-Legal Society, the Massachusetts Medico-Legal Society, the Société de Chemie de Paris, Société de Chimie Industrielle, and a fellow of the New York Academy of Science. In 1896 he was United States delegate to the International Congress of Applied Chemistry in Paris, in 1900 chairman of the American committee on organization in Paris, and Section X, Berlin, in 1903. He was a collaborator on the Century Dictionary.

Dr. Doremus was born in New York City on September 5, 1851. His wife, Elizabeth Johnson Ward, is a well-known playwright, being author of "The Circus Rider," played around the world by Rosina Volkes, "Fortunes of the King," played by James K. Hackett, and "By Right of Sword," played by Ralph Stewart. Their married life was ideal, but sad to say they lost two sons in infancy. Their only daughter married Park Benjamin, Jr.

Dr. Doremus, like his father, was interested in both the new and the historical in science. He had the first telephone receivers made, and the City College received the historic coils of copper straps, crudely insulated, with which Professor Henry made his classical induction experiments, by hanging one coil on either side of a door. Dr. Doremus made synthetic diamonds here with Henri Moisson, which are now in possession of George F. Kunz. With John W. Draper and his father, he made the first daguerreotypes produced in this country, and was Reporter on Photography for the United States at the Vienna Exposition in 1873.

He served as expert in many patent and criminal cases and his patents cover water softening, a mechanical gas furnace, treatment of kryolith, manufacture of hydrofluoric acid, alumina from clay, and potash from feldspar. He also did notable work in the fields of foods and sanitary chemistry, toxicology, and physiological chemistry. At the time of his death he had just perfected a new method for the production of aluminium.

Dr. Doremus was always the refined and courteous gentleman. His profound and extensive fund of information was often drawn on to aid a friend or to add to a discussion. At college "Charley's grin" was a by-word, and a host will long remember him as teacher, fellow, and friend. Death kindly took him as he slept, and with him there passes in science an honored name and a tradition. *Ave atque vale!*

JEROME ALEXANDER

. . . . . .

At the meeting of the New York Section on January 8, 1926, the following resolution was adopted:

WHEREAS, The members of the New York Section of the AMERICAN CHEMICAL SOCIETY have heard with deep regret of the death of Dr. Charles Avery Doremus, a charter member of the AMERICAN CHEMICAL SOCIETY and of this section, and of the Chemists' Club of New York City, and whereas Dr. Doremus has been for more than fifty years an active worker in chemistry, beginning with his graduation at the College of the City of New York and followed by the degree conferred by the University of Heidelberg and Leipzig, and by the teaching of medical chemistry and toxicology in Bellevue Medical School in New York and in the Medical School of the University of Buffalo, and by prolonged service as assistant professor and professor of chemistry as successor to his father, the late Dr. Robert Ogden Doremus, in the College of the City of New York for twenty-two years, and further, after his retirement from teaching in 1904, in the practice of consulting chemistry in New York City, and in the publication of chemical papers, beginning with an article in the *Proceedings of the American Chemical Society* in 1876, and of later contributions during his life to the *Journal of the American Chemical Society*, and in other chemical journals. Therefore, it is

Resolved, That the influence of Dr. Doremus as a teacher and a worker in many fields of chemical interest is long to be remembered and that the members of this section hereby express their respect for his memory and esteem for him as a colleague and as a brother in the chemical profession.

Resolved further, That the sympathy and condolence of the members of this section be extended to the relatives and friends of Dr. Doremus and that these resolutions be recorded in the archives of this section and that a copy of the same be presented to the widow of our deceased member.

BOOK REVIEWS

The Conversion of Coal into Oils. By Franz Fischer. Translated from the German by R. Lessing. xiii + 284 pages. 75 illustrations. $7^1/_2 \times 9^3/_4$ inches. Ernest Benn, Ltd., London, 1925. Price, 36 s.

English-speaking chemists and fuel technologists owe a real debt of gratitude to Dr. Lessing for his excellent translation of Dr. Fischer's timely account of the important fuel researches conducted at the Kaiser Wilhelm Institut für Kohlenforschung at Mülheim-Ruhr in Germany during the last ten years.

Five methods of obtaining oil from coal are discussed in chapters as follows: Chapter I, Extraction by Solvents, briefly refers to the important literature on the identification of chemical compounds in coal extracts, and concludes that no practical application can be made of such methods for obtaining oil from coal at ordinary temperatures where no thermal decomposition occurs. Chapter II, Production and Working Up of Primary Tar, deals principally with the work of Fischer and associates on the low-temperature distillation of German bituminous and brown coals in the Fischer laboratory rotary retort, the composition and yields of the gases, oils, tars, and semicoke obtained, and the utilization of these products. Chapter III, Hydrogenation of Coal, reviews the work of Berthelot and of Bergius, and the experiments by the author on direct and indirect hydrogenation by means of sodium formate, by carbon monoxide and water, and by sodium carbonate and hydrogen. Chapter IV, Synthetic Processes, is of particular interest because of the recent commercial success in synthesizing methanol from carbon monoxide and hydrogen. The Mülheim experiments on production of liquid products from carbon monoxide and hydrogen at various temperatures and pressures, and in the presence of various catalysts, are described in considerable detail. An excellent review of the literature in this field is also included. Chapter V, Hydrocarbons from Carbides, reviews briefly the literature and possibilities of this route of coal to oil. Lessing concludes the book with an appendix on recent developments in low-temperature carbonization.

Of special interest to chemists is the large part of Chapter II that is devoted to the working up of primary tar, in particular the experiments on the reduction of higher phenols to benzene and toluene, and the cracking and hydrogenation of primary tar.

The translator is to be congratulated in preserving the author's personal style of expression and yet giving a smooth and clear English translation. The type is large and the editorial make-up is excellent. No one interested in the problem of oil from coal or the constitution of coal can afford to be without this book.

A. C. Fieldner

The Oil Industry. By Ernest Raymond Lilley. 548 pages. 181 figures, 43 tables. D. Van Nostrand Co., New York, 1925. Price, $6.00.

This book covers in a general way the entire field of the petroleum industry, including the four main branches of production, transportation, refining, and marketing. As must necessarily be the case in a book of this size, it is possible to go into but little detail on any subject. The author attempts to present a picture of the industry as a whole for the benefit of the workers in its specialized branches and for the benefit of those interested in the industry because of investments.

In the main this effort is fairly successful. The principal criticism of the book is the elaboration of the sections dealing with the problems of production and transportation at the expense of refining. The entire section dealing with refining, cracking, and blending and compounding comprises only 70 pages. To one acquainted with the technical problems of this branch it is surprising to note that "in theory distillation is simple," even though the author admits that "in practice it is complicated." No mention of fractional distillation is made and the only mention of fractionating towers is quite misleading as to their general use for fractionation. There is also the natural tendency to elaborate the description of those processes or pieces of equipment on which there is much published material to the neglect of more important and common, but less well advertised, operations.

More detailed attention is given to the subjects of oil lands and leasing, lease operation, and foreign leases and concessions, much valuable information being brought together here in instructive although necessarily condensed form.

The book makes no pretense of furnishing physical constants, design data, or such other information as is available in the various handbooks. It is descriptive in character and written in interesting style. It should prove of greatest value to those familiar with manufacturing operations but who desire information in regard to the other branches of the industry.

N. E. Loomis

Organic Syntheses. An Annual Publication of Satisfactory Methods for the Preparation of Organic Chemicals. Vol. V. By Carl Shipp Marvel, Editor-in-Chief. 110 pages. John Wiley & Sons, Inc., New York, 1925. Price, $1.50.

The appearance of each new volume in this excellent series is always an event among organic chemists. The high standard characteristic of the preceding volumes issued during the past four years has been maintained in Volume V. Thirty-three distinct preparations covering a wide range of classes of organic compounds are described with the precision customary in these publications. Some of the compounds are old friends while others will be new acquaintances to most organic chemists. Thus, the names ethyl oxalate and benzalaniline have a familiar ring, while cyclohexene oxide and cyclopentanone are at least only speaking acquaintances.

The authors are to be congratulated upon the success of their latest venture.

Lauder W. Jones

National Directory of Commodity Specifications. Department of Commerce, *Bureau of Standards Miscellaneous Publications* **65**, August 28, 1925. 379 pages. Sold only by the Superintendent of Documents, Government Printing Office, Washington, D. C. Price, $1.25.

The general features of this list of about 27,000 specifications have been noted [This Journal, **17**, 1013 (1925)] in a statement prepared from a circular issued by the Department of Commerce. The book is well worth more than its price to any one who has use for such a list.

It is probably nearly as useful as it would have been if time had been taken to classify the specifications carefully and to arrange them in a systematic manner under suitable headings. The titles are grouped under numbered headings, but the arrangement within the groups does not appear to follow any regular plan.

A number of specifications are listed in more than one group. A specification for No. 5 olive drab sash cord is given under No. 302.46, Sash Cord, and also under 715.4, Wires, Cords, and Cables (telephone cords, cables, etc.). Cover glasses come under No. 526.3, Cover Glasses in the general class of Glass and Glass Products, and also under 918.2, Beakers, Glasses, Graduates, and Funnels. Nessler jars appear with ointment jars and battery jars under No. 955.4, Jars, in the general class of containers, and Hessler (one of the very few misprints in the book) color comparison tubes (50 and 100 cc.) are under No. 918.7, Tubes and Tubing. Group No. 505.29, Miscellaneous Specifications for Road Oils includes as consecutive items heavy road oil, calcium chloride, light dust-laying oil, calcium chloride. No. 834.8, Caustic Soda (or Lye) includes caustic soda, sodium hydroxide (reagent), sodium phosphate (reagent), sodium sulfite (reagent), sodium thiosulfate (reagent), caustic soda (for soap manufacture), lye. The phosphate, sulfite, and thiosulfate do not appear under 834.9, Other Sodium Compounds.

A kind of differentiation is indicated by an asterisk placed "at each specification formulated by the national technical societies, the trade associations having national recognition, and other organizations which speak for industry or with the authority of the Federal Government as a whole." Most of the specifications so marked meet the requirement of the first sentence of the foreword by Secretary Hoover: "Specifications are the formulated, definite, and complete statements of what the buyer requires of the seller." Many of the items not so marked also come up to this standard, particularly the specifications used by the

railroads. A large number of the unmarked items, however, are specifications in name only. They have been prepared for some purchasing agency that demanded a specification, whether it could be made or not. The result is something that reads rather like a specification, but leaves requirements and methods of inspection and test quite indefinite. Others have been prepared to look like general specifications, while really requiring a particular brand or make of the article described. A number of obsolete specifications are also included. Listing of such specifications is necessary in a publication like the directory. They will doubtless be omitted from the proposed encyclopedia which is to be issued in loose-leaf form and include actual specifications or abstracts. Those of the 27,000 that get into the encyclopedia will probably approach the standard of the 339 United States Government Master Specifications promulgated by the Federal Specifications Board up to October 1, 1925.

W. D. COLLINS

Chemistry and Civilization. BY ALLERTON S. CUSHMAN. 2nd edition. 171 pages. E. P. Dutton & Co., New York, 1925. Price, $2.50.

Those who have read the previous edition of this brief sketch of the progress of chemistry need now read only the last chapter of the new edition. The first six chapters are reprints—and although some of them might well have been revised to include the developments of the past five years, the book is, after all, for the layman, and for him the latest development has not of itself special significance. The volume as a whole makes a very readable and interesting story. While the scope of the discussion does not permit the presentation of any theories or explanations other than those generally accepted, the rather dogmatic presentation is a bit unfortunate. The intelligent layman should not be given the impression that any of the theories of chemistry, or of science in general, are so completely developed and so universally accepted as to be no longer subject to revision. The fate of the phlogiston theory would have served admirably to illustrate what may some day happen to many of our present-day theories.

A new chapter, entitled Modern Concepts of Matter and Energy, constitutes the principal difference between the former and present editions of the book, and much may be said in commendation of it. The clear presentation of so intricate a subject as "the astronomy of the atom" is difficult at best and when one does this in nontechnical language so that the intelligent layman can follow and understand "what it is all about," it is no mean accomplishment. At the top of page 138 a typographical error ascribes to the average electron a period of 2×10^{15} seconds in which to revolve around its proton.

HARDEE CHAMBLISS

The Bureau of Standards. Its History, Activities, and Organization. Service Monograph 35 of the United States Government. BY GUSTAVUS A. WEBER. Compiled and issued by the Institute for Government Research. 299 + xv pp. Johns Hopkins Press, Baltimore, 1925. Price, $2.00.

The history, activities, and organization of the Bureau of Standards constitute the subject matter of this monograph and considerable detail is condensed from the many sources listed in the bibliography. The history begins with the old office of Standard Weights and Measures of the Treasury Department and traces in an interesting manner the development of this important bureau down to the date of publication. Under the discussion of the activities of the bureau, care has been taken to describe, not only the principal divisional enterprises, but many of the individual problems and instances of coöperation with business organizations and with individuals. In the section on organization the purposes of the various divisions and sections are outlined, together with a statement of the number of employees engaged in such special work, the number and grade of personnel in each unit, and the annual salary rate. Further, there is a classification of activities, a chapter on publications, and a useful compilation of laws which apply to the Bureau of Standards, beginning with those applying to the Bureau of Weights and Measures and including the act to establish a national Bureau of Standards and such supplementary acts as apply to its work. The act of March 3, 1901, states in Section 2:

> That the functions of the bureau shall consist in the custody of the standards; the comparison of the standards used in scientific investigations, engineering, manufacturing, commerce, and educational institutions with the standards adopted or recognized by the Government; the construction, when necessary, of standards, their multiples and subdivisions; the testing and calibration of standard measuring apparatus; the solution of problems which arise in connection with standards; the determination of physical constants and the properties of materials, when such data are of great importance to scientific or manufacturing interests and are not to be obtained of sufficient accuracy elsewhere.

This monograph would seem to fulfil the purposes of this series, which are to give the history of the establishment and development of the several branches of government service, outline the functions of each, indicate the organization and character of plant, compile laws and regulations governing its operation, present the financial statement showing appropriations and expenditures, and finally present a full bibliography of sources of information, official and private, bearing on the service and its operations.

Volatile Solvents and Thinners. BY NOËL HEATON. Oil & Colour Chemistry Monographs, edited by R. S. MORRELL. 154 pages. D. Van Nostrand Co., New York, 1926. Price, $4.50.

The enormous development in the lacquer industry in America during the last few years has stimulated considerable interest in the manufacture and use of organic solvents. Up to six months ago there was practically no book covering this field published in English. Two books have appeared in a monograph series from England. One of these books is "Volatile Solvents and Thinners."

On reading this delightfully written little treatise, the reviewer was impressed with the fact that the lacquer industry has not been developed in England to anywhere near the extent that it has been developed in this country. Furthermore, the English writers do not seem to be thoroughly familiar either with the manufacture on a commercial scale or the use of the more modern solvents.

This book has very excellent chapters on Coal Tar Hydrocarbons and the Terpene Group. The subject matter concerning the Alcohol Group, Ketones and Ethers, and Esters is far from complete, and in some cases, from the reviewer's standpoint, is inaccurate. The author seems to have made a rather thorough literature search through the trade journals and quoted statements presumably written by salesmen who are desirous of throwing the most favorable light upon their products. This has naturally given him a rather biased viewpoint, and apparently these statements were not checked by the author by personal investigation. This, of course, detracts from the value of the book and will probably cause it to become obsolete as other and more accurate information is published in the near future.

The reviewer would suggest that it might be beneficial for English writers who are contemplating publishing books on the subject of organic solvents and lacquers to make a trip to America and see first hand most of the processes for the manufacture of these solvents and also their utilization in lacquers. Information obtained in this way would be much more accurate than that obtained by conversation with promoters and salesmen or given in articles found in trade journals. Furthermore, a trip to this country and an investigation of this new lacquer industry would probably mean much to the development of the lacquer industry in England, and it certainly would prevent a duplication of research and development work.

In spite of the lack of authentic information, this book is a very attractive and readable treatise and should prove of interest to the technical man not only in England but also in this country.

D. B. KEYES

Manuel du Chimiste de Laiterie Analysis de Lait et de ses Sous-Produits. BY F. LABARRE. 168 pages. Gauthier-Villars & Cie., Paris, 1925. Price, 20 francs.

This small book covers various phases of the analysis of milk and milk products. The book is very much condensed. The methods are given in but very slight detail and consequently are of no great value to one who is unfamiliar with the chemistry of milk and its by-products. To those familiar with this subject the book affords nothing of very great value. There are many books in the English language which are preferable.

There are practically no references to original sources of the methods and the analyses quoted are mean analyses with very few references to the extremes. The Babcock method, universally used in the United States, is conspicuous by its absence, although the Gerber method is described in very good detail. Most of the up-to-date methods, however, are mentioned, but very little of value is given on the interpretation of results.

H. C. LYTHGOE

Chemistry of Drying Oils. By R. S. Morrell and H. R. Wood. Oil and Colour Chemistry Monographs. 224 pages. D. Van Nostrand Co., New York, 1925. Price, $4.50.

This book is well written. It is an exceedingly interesting and valuable book for those connected with the paint, varnish, linoleum, and printing ink industries. It is very clear and goes into the chemistry of drying oils rather more completely than any previous work. The chapter on Boiled, Blown and Stand Oil is of great value to the paint chemist. The chapters on Bleaching and Drying contain information which is up to date.

This book should be in the library of every paint, varnish, linoleum, and printing ink manufacturer, as it contains most excellent data.

It has two indexes, one for subjects and one for names, which is an additional convenience.

Maximilian Toch

Pyroxylin Enamels and Lacquers. By Samuel P. Wilson. 213 pages. D. Van Nostrand Co., New York, 1925. Price, $3.00.

This handbook is the first authoritative exposition of the new industry and is written with refreshing candor. Its style is admirably simple and it contains no more than the usual quota of first-edition typographical errors. The whole work is intensely practical in aspect. In fact, the absence of an adequate discussion of the physico-chemical principles underlying the selection of solvents on the basis of their rates of evaporation, their chemical structure, and their properties in constant boiling mixtures is to be regretted. Further, it is felt that the brief discussion on page 55 of the formulation problems encountered in blending solvent and nonsolvent to secure compatibility and to prevent cotton blush and gum blush is too brief and obscure to be very helpful to the novice.

Part I, dealing with Raw Materials, is distinctly the weaker of the two parts. This is particularly noticeable in the chapter on Solvents, where errors of fact have crept in. The yield of butanol by fermentation as given by the author is about 200 per cent of the theoretical. Contrary to his opinion, the use of molasses as a raw material in this process will not reduce butanol to a price comparable with ethyl alcohol, as can readily be seen if the available carbohydrate in corn and molasses is considered. Many will disagree with the classification of camphor and diethyl phthalate as solvents rather than as temporary plasticizers. Cyclohexanol is listed as a solvent and its peculiar blending power for mixtures of true solvents with nonsolvents is not mentioned. Chapter VII, on Pigments, is particularly meritorious.

Part II covers, fairly completely, all the operations necessary in the manufacture of lacquer. The different types of present-day lacquer are defined by their properties and uses, and numerous formulas are given. The author has a habit, that will probably distress many who attempt to follow his formulas, of stating gum content, not as solid material, but as a "solution." "Ester gum solution" is frequently mentioned, whereas on page 83 ester gum is stated to be used in "proportions of 6, 8, and 10 pounds per gallon," several different solvent mixtures being mentioned. Similar comments might be made concerning the use of such terms as "shellac in butanol" and "Elemi solution." Kauri gum unfortunately is not used in any of the typical formulas.

Analytical methods for lacquer have not kept pace with production and this is reflected in Chapter XII.

Bruce K. Brown

Erkennung und Prüfung von Färbungen. By W. Zänker and H. Rettberg. 80 pages + 18 tests. A. Ziemsen Verlag, Wittenberg, Berlin, 1925. Price, 5 marks.

This is a nicely arranged book dealing with the testing of colors on dyed fabrics, both for the purpose of determining the qualities of fastness and for identifying the class of the dyestuffs employed. With the customary German methodical mind in developing a treatise in any field, a history of the entire subject is first given, after which the authors proceed to a systematic investigation of the matters in hand. Clear and concise descriptions are given of the latest and most improved methods of testing the various qualities of fastness of the colors as dyed on different kinds of fabric materials. These methods include a great deal of work that has been developed subsequent to the war, so this volume may be said to give perhaps the latest knowledge on this subject. It must be borne in mind, however, that the methods and materials have a distinct reference to the special technic of German trade. For a full use in this country the book would have to be supplemented with material that would apply more specifically to the fabrics and dyes that are employed here.

The tests for determining the nature of the coloring matters used in the production of the dyed colors are probably of more interest to American practice than the fastness tests. Several important new forms of testing are included, such as the paraffin test for fast colors on cotton, particularly as employed in conjunction with the hydrosulfite test. There is also a section on the testing for the naphthol A-S dyes, which is an important addition to our knowledge on this subject. The tests for the vat colors are also thoroughly discussed and are of the utmost importance to cotton dyers. In fact, this volume may be said to deal almost entirely with cotton colors, for although there are a few pages devoted to the testing of dyes on animal fibers, this subject is taken up in a very brief and cursory manner. Plenty of examples and a good index are given, and the book is well worth the attention of all cotton dyers.

J. M. Matthews

New Books

Anleitung für das Pratikum in der Gewichtsanalyse. R. Weinland. 3rd edition, revised and enlarged. 132 pp. Theodor Steinkopff, Dresden and Leipzig. Price, 6 marks.

Applied Chemistry. A Practical Handbook for Students of Household Science and Public Health. C. K. Tinkler and Helen Masters. Vol. II—Foods. 276 pp. Crosby Lockwood & Son, London. Price, 15 s. net.

Chemische Technologie der Leichtmetalle und Ihrer Legierungen. F. Regelsberger. Chemische Technologie in Einzeldarstellungen, edited by A. Binz. 385 pp. Otto Spamer, Leipzig. Price, paper, 26 goldmarks; bound, 29.

Fabrication des Ferro-Alliages. A. Coutagne. Encyclopédie Minière et Métallurgique, published under the direction of L. Guillet. 650 pp. J. B. Baillière et Fils, Paris. Price, 60 francs.

Fabrikation der Soda. H. Molitor. 231 pp. Max Jänecke Verlagsbuchhandlung, Leipzig. Price, paper, 11.60 marks; bound, 13.10.

Industrial Museum. Charles R. Richards. 117 pp. Illustrated. The Macmillan Co., New York. Price, $3.00.

Introduction to the Physics and Chemistry of Colloids. Emil Hatschek. 5th edition. 183 pp. P. Blakiston's Son & Co., Philadelphia. Price, $2.25.

Intermediates for Dyestuffs. A. Davidson. 256 pp. E. Benn, Ltd., London. Price, 36 s.

Laboratory Exercises in General Chemistry. William Foster and H. W. Heath. 186 pp. D. Van Nostrand Co., New York. Price, $1.25.

Laboratory Manual of Elementary Colloid Chemistry. Emil Hatschek. 2nd edition. 153 pp. P. Blakiston's Son & Co., Philadelphia. Price, $2.00.

Leitfaden der Kolloidchemie für Biologen und Mediziner. Eine Einführung in die Allgemeine Physiologie, Pathologie, Pharmakologie. H. Handovsky. 2nd edition, revised. Theodor Steinkopff, Dresden and Leipzig. Price, paper, 12 marks; bound, 14.

Metallurgy and Its Influence on Modern Progress. With a Survey of Education and Research. Sir R. A. Hadfield. 388 pp. Chapman & Hall, Ltd., London. Price, 25 s.

Méthodes Physiques Appliqués à la Chimie. P. Job. Collection de Physique et Chimie. 251 pp. Librairie Octave Doin, Paris. Price, 30 francs.

Oxydation und Reduktion. Handbuch der Biologischen Arbeitsmethoden. Abt. I—Chemische Methoden, Teil. 2, Heft I. Richard Stoermer. 456 pp. Urban & Schwarzenberg, Berlin. Price, 21 marks.

Practical Photo-Micrography. J. E. Barnard and F. V. Welch. 2nd edition. 316 pp. Edward Arnold & Co., London. Price, 18 s.

Seventh Annual Convention of the National Lime Association and Twenty-third Annual Meeting of Lime Manufacturers. Technical Papers and Addresses. 85 pp. National Lime Association, Washington, D. C.

Spectroscopy of X-Rays. M. Siegbahn. Translated by G. A. Lindsay. 287 pp. Oxford University Press, London. Price, 20 s.

Scottish Shale Industry. Report by Accountants Appointed by the Board of Trade on the Costs of Production and Financial Results in the Shale Industry Carried on by the Undertakings Associated with Scottish Oils, Ltd. 14 pp. H. M. Stationery Office, London. Price, 3 d. net.

Technical Education, Its Development and Aims. C. T. Millis. 182 pp. E. Arnold & Co., London. Price, 6 s.

Text-Book of Pharmaceutical Chemistry. A. O. Bentley and J. E. Driver. 456 pp. Oxford University Press, London. Price, 18 s.

GOVERNMENT PUBLICATIONS

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.*

Bureau of Foreign and Domestic Commerce

Market for Spraying and Dusting Equipment in Bulgaria. *Special Circular* **S-48,** Agricultural Implements Division. 2 pp. Issued January 11, 1926.

Same. Chile. *Special Circular* **S-45,** Agricultural Implements Division. 3 pp. Issued January 5, 1926.

Same. Great Britain. *Special Circular* **S-41,** Agricultural Implements Division. 3 pp. Issued December 21, 1925.

Same. Greece. *Special Circular* **S-46,** Agricultural Implements Division. 2 pp. Issued December 31, 1925.

Same. Irish Free State. *Special Circular* **S-42,** Agricultural Implements Division. 3 pp. Issued January 4, 1926.

Same. Lithuania. *Special Circular* **S-43,** Agricultural Implements Division. 2 pp. Issued January 5, 1926.

Same. Portugal. *Special Circular* **S-44,** Agricultural Implements Division. 3 pp. Issued January 5, 1926.

Synthetic Camphor Industry. *Special Circular* **122,** Chemical Division. 2 pp. Issued January 5, 1926.

World Trade Notes on Chemicals. *Circular* **74-A,** Chemical Division. 2 pp. Issued December 19, 1925.

World Trade Notes on Fertilizers. *Circular* **74-E,** Chemical Division. 1 p. Issued December 19, 1925.

Same. *Circular* **75-E,** Chemical Division. 2 pp. Issued January 2, 1926.

World Trade Notes on Industrial Chemicals. *Circular* **75-A,** Chemical Division. 2 pp. Issued January 2, 1926.

Bureau of Mines

Consumption of Explosives in November, 1925. W. W. Adams. *Reports of Investigations* **2723.** 9 pp. Issued December, 1925.

Review of Safety and Health Conditions in the Mines at Butte. G. S. Rice and R. R. Sayers. *Bulletin* **257.** 29 pp. Paper, 10 cents.

Salt, Bromine, and Calcium Chloride in 1924. K. W. Cottrell. *Mineral Resources of the United States, 1924.* Part II, pp. 141–9. Issued December 15, 1925. Paper, 5 cents.

Slate in 1924. G. F. Loughlin and A. T. Coons. *Mineral Resources of the United States, 1924.* Part II, pp. 151–60. Paper, 5 cents.

Bureau of Standards

Abridged Volume Correction Table for Petroleum Oils. Supplement to *Circular* **154.** 4 pp. Issued October 8, 1925. Paper, 5 cents.

Annual Report of Director of the Bureau of Standards for Fiscal Year Ended June 30, 1925. *Miscellaneous Publications* **69.** 41 pp. Paper, 5 cents.

Dielectric Constant, Power Factor, and Resistivity of Rubber and Gutta-Percha. H. L. Curtis and A. T. McPherson. *Technologic Paper* **299.** 54 pp. Paper, 20 cents.

Congress

Alcohol. A Bill to amend the National Prohibition Act, to provide for a Bureau of Prohibition in the Treasury Department, to define its powers and duties, and to place its personnel under the Civil Service Act. Introduced by Mr. Cramton, December 7, 1925. *H. R.* **394.** 8 pp.

Calcium Arsenate. A Bill to transfer calcium arsenate from the dutiable to the free list. Introduced by Mr. Vinson of Georgia. December 7, 1925. *H. R.* **3984.** 1 p.

Chemicals and Dyestuffs. Resolution to investigate the means and methods of control and production of chemicals and dyestuffs, and for other purposes. Introduced by Mr. Frear, January 6, 1926. *H. Res.* **75.** 1 p.

Copper. A Bill to amend the Tariff Act of 1922, entitled "An Act to provide revenue, to regulate commerce with foreign countries, to encourage the industries of the United States, and for other purposes." Introduced by Mr. Cameron, January 4, 1926. *S.* **2018.** 3 pp.

Corrosive Substances. A Bill to safeguard the distribution and sale of certain dangerous caustic or corrosive acids, alkalies, and other substances in interstate and foreign commerce. Introduced by Mr. Pepper, January 7, 1926. *S.* **2320.** 12 pp.

Metric Weights and Measures. A Bill extending the use of metric weights and measures in merchandising. Introduced by Mr. Britten. December 7, 1925. *H. R.* **10.** 3 pp.

Muscle Shoals. A Bill to provide for the operation of Dam Numbered 2 at Muscle Shoals, Ala., for the construction of other dams on the Tennessee River and its tributaries, for the incorporation of the Federal Power Corporation, and for other purposes. Introduced by Mr. Norris, January 5, 1926. *S.* **2147.** 16 pp.

Same. Concurrent Resolution establishing a joint committee on Muscle Shoals. Introduced by Mr. Snell, January 4, 1926. *H. Con. Res.* **4.** 2 pp. [Report 36] Passed the House of Representatives January 5, 1926.

Same. Joint Resolution establishing a joint congressional committee to conduct negotiations for a private lease of the properties owned by the United States at Muscle Shoals, Ala., and to report its findings with recommendations as to acceptance thereof. Introduced by Mr. Madden, December 10, 1925. *H. J. Res.* **59.** 2 pp.

Same. Joint Resolution to suspend the jurisdiction, power, and authority of the Federal Power Commission to issue licenses on the Tennessee River and its tributaries until the Congress has taken final action for the control, operation, or disposition of Dam Numbered 2 on said river, at Muscle Shoals, Ala. Introduced by Mr. Norris, January 4, 1926. *S. J. Res.* **35.** 2 pp.

Pollution of Rivers. A Bill to prevent the pollution by oil of navigable rivers of the United States. Introduced by Mr. Wilson of Louisiana, December 14, 1925. *H. R.* **5382.** 3 pp.

Same. Introduced by Mr. Ransdell, December 15, 1925. *S.* **1717.**

Same. To amend an Act entitled "An Act making appropriations for the construction, repair, and preservation of certain public works on rivers and harbors, and for other purposes," approved March 3, 1899, by adding a new section thereto forbidding deposit of noxious acids and acid materials in the navigable waters of the United States. Introduced by Mr. Appleby, December 7, 1925. *H. R.* **3786.** 3 pp.

Potash. A Bill authorizing investigation by the United States Geological Survey to determine location and extent of potash deposits in the United States. Introduced by Mr. Hudspeth, December 7, 1925. *H. R.* **3863.** 1 p.

Rubber. Resolution authorizing an investigation of the crude rubber industry. Introduced by Mr. Tilson, December 18, 1925. *H. Res.* **56.** 2 pp.

Same. Resolution directing an investigation of crude rubber and other important raw material. Introduced by Mr. Snell, December 19, 1925. *H. Res.* **59.** 1 p. [Report 24]

Department of Agriculture

Report of the Chemist for the Fiscal Year Ended June 30, 1925. C. A. Browne. 23 pp.

Certification of Coal-Tar Food Colors. *Miscellaneous Circular* **52.** 12 pp. Issued November, 1925. Paper, 5 cents.

Geological Survey

Geology and Coal Resources of the Gallup-Zuni Basin, New Mexico. J. D. Sears. *Bulletin* **767.** 53 pp. Price, 50 cents.

Geology of a Part of Western Texas and Southeastern New Mexico. With Special Reference to Salt and Potash. H. W. Hoots. *Bulletin* **780-B.** *Contributions to Economic Geology, 1925.* Part I, pp. 33–126. Issued December 29, 1925.

Surface Water Supply of the United States, 1923. Part I—North Atlantic Slope Drainage Basins. N. C. Grover, C. H. Pierce, A. W. Harrington, O. W. Hartwell, and A. H. Horton. *Water-Supply Paper* **561.** 294 pp. Paper, 35 cents.

Public Health Service

Some Properties of Iron Compounds and Their Relation to Water Clarification. L. B. Miller. Reprint 1023 from *Public Health Reports.* 8 pp. Paper, 5 cents.

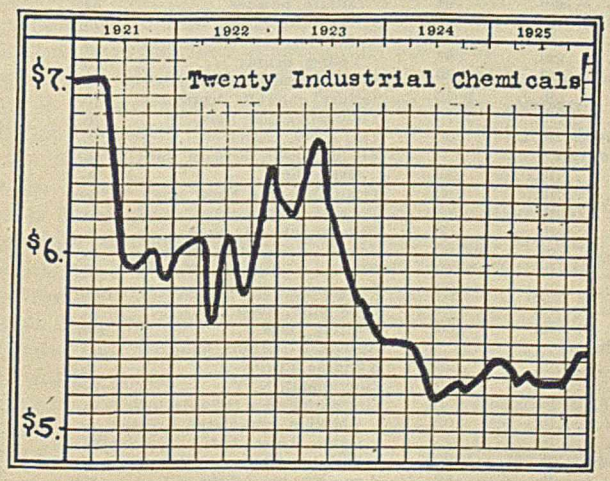
Stream Pollution by Wastes from By-Product Coke Ovens. A Review, with Special Reference to Methods of Disposal. R. D. Leitch. Reprint 1042 from *Public Health Reports.* 6 pp. Price, 5 cents.

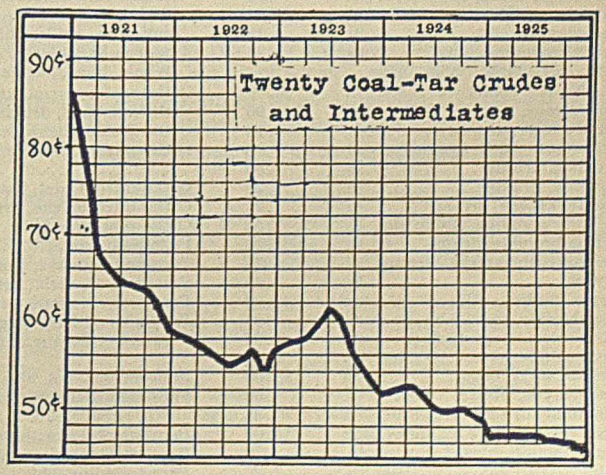
The Tenth Revision of the United States Pharmacopœia. G. B. Roth. *Public Health Reports* **40** (December 25, 1925), 2867–72.

MARKET REPORT—JANUARY, 1926

FIRST-HAND PRICES FOR CHEMICALS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET ON JANUARY 15

Acetanilide, tech., bbls.	lb.	.27
U. S. P., bbls.	lb.	.35
Acetic anhydride, 92–95%, cbys.	lb.	.29
Acetone, C. P., drums, wks.	lb.	.13
Acetophenetidine, bbls.	lb.	1.85
Acid, Acetic, 28%, c/1. bbls.	100 lbs.	3.24
56%, c/1. bbls.	100 lbs.	6.09
Glacial, c/1. bbls.	100 lbs.	11.47
Acetylsalicylic, bbls.	lb.	.72½
Anthranilic, 99–100%, drums.	lb.	.98
Benzoic, tech., bbls.	lb.	.57
Boric, bbls.	lb.	.09½
Butyric, 60%, pure, 5-lb. bot.	lb.	.55
Chloroacetic, mono-, bbls., wks.	lb.	.25
Di-, cbys.	lb.	1.00
Tri-, bbls.	lb.	2.50
Chlorosulfonic, drums, wks.	lb.	.15
Chromic, pure, 98%, drums.	lb.	.37
Chromotropic, bbls.	lb.	1.35
Cinnamic, 5-lb. cans.	lb.	3.25
Citric, U. S. P., kegs, bbls.	lb.	.46
Cresylic, pale, drums	lb.	.58
Formic, 85%, cbys., N. Y.	lb.	.10
Gallic, U. S. P., bbls.	lb.	.65
Glycerophosphoric, 25%, 1-lb. bot.	lb.	1.85
H, bbls., wks.	lb.	.68
Hydriodic, 10%, U. S. P., 5-lb. bot.	lb.	.65
Hydrobromic, 48%, cbys., wks.	lb.	.45
Hydrochloric, 20°, tanks, wks.	100 lbs.	1.00
Hydrofluoric, 30%, bbls., wks.	lb.	.06
60%, bbls., wks.	lb.	.13
Hydrofluosilicic, 35%, bbls., wks.	lb.	.10
Hypophosphorus, 30%, U. S. P., 5-gal. demis.	lb.	.36
Lactic, 22%, dark, bbls.	lb.	.05½
66%, light, bbls., wks.	lb.	.26
Metanilic, bbls.	lb.	.60
Mixed, tanks, wks.	N unit	.06
	S unit	.01
Molybdic, 85%, kegs	lb.	1.25
Naphthionic, tech., bbls.	lb.	.55
Neville & Winther's, bbls.	lb.	.95
Nitric, C. P., cbys.	lb.	.12
Nitric, 38°, c/l. cbys., wks.	100 lbs.	5.25
Oxalic, bbls., wks.	lb.	.10¾
Phosphate, bulk	ton	9.50
Phosphoric, 50%, cbys.	lb.	.07
Picramic, bbls.	lb	.50
Picric, bbls.	lb.	.30
Pyrogallic, tech., bbls.	lb.	.85
Salicylic, tech., bbls.	lb.	.33
Stearic, d. p., bbls.	lb.	.15¾
Sulfanilic, 250-lb. bbls.	lb.	.15
Sulfuric, 66°, c/l. cbys., wks.	100 lbs.	1.25
66°, tanks, wks.	ton	14.00
60°, tanks, wks.	ton	10.00
Oleum, 20%, tanks, wks.	ton	17.00
40%, tanks, wks.	ton	40.00
Sulfurous, U. S. P., 6%, cbys.	lb.	.05
Tannic, tech., bbls.	lb.	.30
Tartaric, U. S. P., cryst., bbls.	lb.	.29
Tobias, bbls.	lb.	.85
Tungstic, kegs	lb.	1.00
Valeric, C. P., 10-lb. bot.	lb.	2.50
Alcohol, U. S. P., 190 proof, bbls.	gal.	4.94
Amyl, 10%, Imp. drums	gal.	1.70
Butyl, drums, wks.	lb.	.19
Cologne Spirit, bbls.	gal.	5.04
Denatured, No. 5, Comp. denat., drs.	gal.	.40
No. 6, Comp. denat., drs.	gal.	.52½
No. 1, Spec. denat., drs.	gal.	.53½
Isobutyl, ref., drums	lb.	1.10
Isopropyl, ref., drums	gal.	1.00
Propyl, ref., drums	lb.	.75
Wood, *see* Methanol		
Alpha-naphthol, bbls.	lb.	.65
Alpha-naphthylamine, bbls.	lb.	.35
Alum, ammonia, lump, bbls., wks.	100 lbs.	3.15
Chrome, casks, wks.	100 lbs.	5.25
Potash, lump, bbls., wks.	100 lbs.	3.50
Soda, bbls., wks.	100 lbs.	3.50
Aluminium, metal, N. Y.	lb.	.28
Aluminium chloride, anhyd., drums	lb.	.35
Aluminium stearate, 100-lb. bbl.	lb.	.22
Aluminium sulfate, comm'l bags, wks.	100 lbs.	1.40
Iron-free, bags, wks.	100 lbs.	2.00
Amidopyrine, boxes	lb.	4.60
Aminoazobenzene, 110-lb. kgs.	lb.	1.15
Ammonia, anhydrous, cyl., wks.	lb.	.13
Ammonia water, 26°, drums, wks.	lb.	.03
Ammonium acetate, kegs	lb.	.43
Bifluoride, bbls.	lb.	.21
Bromide, 50-lb. boxes	lb.	.53
Carbonate, tech., casks	lb.	.08¾
Chloride, gray, bbls.	lb.	.06½
Lump, casks	lb.	.11½
White, bbls.	lb.	.05½
Iodide, 25-lb. jars	lb.	5.20
Lactate, bbls.	lb.	.15
Nitrate, tech., cryst., bbls.	lb.	.21
Oxalate, kegs	lb.	.35
Persulfate, cases	lb.	.21
Phosphate, dibasic, tech., bbls.	lb.	.18
Tribasic, bbls.	lb.	.04
Sulfate, bulk, wks.	100 lbs.	2.70
Thiocyanate, tech., kegs	lb.	.40
Amyl acetate, tech., drums	lb.	2.35
Aniline oil, drums	lb.	.16
Anthracene, 80–85%, casks, wks.	lb.	.60
Anthraquinone, subl., bbls.	lb.	.95
Antimony, metal	lb.	.24
Antimony chloride, anhyd., drums	lb.	.16
Oxide, bbls.	lb.	.19
Salt, Dom., bbls.	lb.	.18
Sulfide, crimson, bbls.	lb.	.25
Golden, bbls.	lb.	.15
Vermilion, bbls.	lb.	.48
Tartrolactate, bbls.	lb.	.45
Argols, red powder, bbls.	lb.	.06½
Arsenic, metal, kegs	lb.	.45
Red, kegs, cases	lb.	.12
White, cases, bbls.	lb.	.03¼
Asbestine, bulk, c/l.	ton	16.00
Barium carbonate, bbls., bags, wks.	ton	44.00
Chloride, bbls., bags, wks.	ton	60.00
Dioxide, bbls., wks.	lb.	.13
Hydroxide, bbls.	lb.	.04½
Nitrate, casks	lb.	.07½
Barium sulfocyanide, 400-lb. bbls.	lb.	.30
Barytes, floated, 350-lb. bbls., wks.	ton	26.00
Benzaldehyde, tech., drums	lb.	.65
F. F. C., cbys.	lb.	1.30
U. S. P., cbys.	lb.	1.15
Benzene, pure, tanks, mills	gal.	.23
Benzidine base, bbls.	lb.	.72
Benzoyle chloride, carboys	lb.	1.00
Benzyl acetate, cbys.	lb.	1.30
Alcohol, 5-liter bot.	lb.	1.40
Chloride, tech., drums	lb.	.25
Beta-naphthol, bbls.	lb.	.24
Beta-naphthylamine, bbls.	lb.	.63
Bismuth, metal, cases	lb.	3.50
Bismuth nitrate, 25-lb. jars	lb.	2.35
Oxychloride, boxes	lb.	4.00
Subnitrate, U. S. P., 25-lb. jars	lb.	3.35
Blanc fixe, dry, bbls.	ton	75.00
Bleaching powder, drums, wks.	100 lbs.	2.00
Bone ash, kegs	lb.	.06
Bone black, bbls.	lb.	.08¼
Borax, powd., bbls.	lb.	.05





Bordeaux mixture, bbls.	lb.	.11¾
British gum, com., c/l.	100 lbs.	4.17
Bromine, bot.	lb.	.47
Bromobenzene, drums	lb.	.50
Bromoform, 5-lb. bot.	lb.	1.65
Butyl acetate, 100-gal. drums	gal.	1.84
Cadmium bromide, 50-lb. jars	lb.	1.20
Cadmium, metal, boxes	lb.	.70
Cadmium sulfide, cs.	lb.	1.20
Caffeine, U. S. P., 5-lb. cans	lb.	3.75
Calcium acetate, bags	100 lbs.	3.00
Arsenate, bbls.	lb.	.06
Carbide, drums	lb.	.04¼
Chloride, drums, wks.	100 lbs.	21.00
Lactate, tech., bbls.	lb.	.35
Nitrate, bbls.	ton	50.00
Phosphate, monobas., bbls.	lb.	.07
Tribas., bbls.	lb.	.11
Calcium carbonate, tech., bgs.	100 lbs.	1.10
U. S. P., precip., 175-lb. bbl.	lb.	.06½
Camphor, Amer., bbls.	lb.	.84
Jap., cases	lb.	.71½
Crude, cases	lb.	.54
Camphor, monobrom, cs.	lb.	1.85
Caramel, bbls.	gal.	.70
Carbazole, bbls.	lb.	.45
Carbon bisulfide, drums	lb.	.06
Carbon black, cases	lb.	.13
Carbon dioxide, liq., cyl.	lb.	.06
Carbon tetrachloride, drums	lb.	.06½
Casein, tech., bbls.	lb.	.13
Cellulose acetate, cs.	lb.	1.50
Cerium oxalate, kegs	lb.	.35
Chalk, pptd., casks	lb.	.04¼
Charcoal, willow, powd., bbls.	lb.	.06
China clay, imp., bgs.	100 lbs.	15.00
Chloral hydrate, drums	lb.	.60
Chloramine T., 5-lb. bot.	lb.	1.35
Chlorcosane, 5-lb. bot.	lb.	.55
Chlorine, liq., c/l., cyl.	lb.	.05½
Chlorobenzene, mono-, drums	lb.	.07
Chloroform, tech., drums	lb.	.28
Chlorohydrin, anhyd., drums	lb.	.75
Chromium acetate, 20° sol., bbls.	lb.	.05½
Sulfate, bbls.	lb.	.07
Cinchonidine sulfate, 100 oz.	oz.	.35
Coal tar, tanks, bbls., wks.	gal.	.07
Cobalt, metal, kegs	lb.	2.50
Cobalt oxide, bbls.	lb.	2.10
Cod-liver oil, bbls.	bbl.	37.50
Collodion, drums	lb.	.23
Copperas, c/l., bulk	ton	13.00
Copper, metal, elec.	lb.	.14
Copper carbonate, bbls.	lb.	.16¾
Chloride, bbls.	lb.	.28
Cyanide, drums	lb.	.48
Oxide, red, bbls.	lb.	.16½
Sulfate, bbls.	lb.	.04⅜
Cotton, soluble, bbls.	lb.	.40
Cream tartar, bbls.	lb.	.22
Cyanamide, bulk, N. Y.	Ammon. unit	1.90
Diaminophenol, kegs	lb.	3.80
Dianisidine, kegs	lb.	3.50
Dichlorobenzene, drums	lb.	.06
Diethylaniline, drums	lb.	.55
Diethylphthalate, drums	lb.	.35
Diethylsulfate, tech., drums	lb.	.20
Dimethylaniline, drums	lb.	.31
Dimethylsulfate, drums	lb.	.45
Dinitrobenzene, drums	lb.	.14½
Dinitrochlorobenzene, bbls.	lb.	.15
Dinitronaphthalene, bbls.	lb.	.32
Dinitrophenol, bbls.	lb.	.32
Diphenylamine, bbls.	lb.	.48
Diphenylguanidine, bbls.	lb.	.95
Epsom salt, tech., bbls., c/l., N. Y.	100 lbs.	2.00
Ether, nitrous, bot.	lb.	.90
Ether, U. S. P., drums	lb.	.16
Ethyl acetate, 99%, drums	gal.	1.15
Bromide, drums	lb.	.50
Chloride, drums	lb.	.26
Methyl ketone, drums	lb.	.27½
Ethyl benzyl aniline, 300-lb. drs.	lb.	1.05
Ethylene bromide, drums	lb.	.70
Chlorohydrin, anhyd., drums	lb.	.75
Glycol	lb.	.30
Feldspar, bulk	ton	20.00
Ferric chloride, tech., bbls.	lb.	.05
Ferrous chloride, cryst., bbls.	lb.	.05
Ferrous sulfide, bbls.	100 lbs.	2.50
Fluorspar, 95%, bags	ton	25.00
Formaldehyde, bbls.	lb.	.09
Formaniline, drums	lb.	.38
Fuller's earth, bags, c/l., mines	ton	15.00
Furfural, 300-lb. bbls.	lb.	.20
Glauber's salt, bbls.	100 lbs.	1.20
Glucose, 70°, bags, dry	100 lbs.	3.24
Glycerol, C. P., drums	lb.	.25
G salt, bbls.	lb.	.50
Hexamethylenetetramine, U. S. P. drums	lb.	.60
Hydrogen peroxide, 25 vol., bbls.	lb.	.07
Hydroquinone, kegs	lb.	1.40
Indigo, 20%, paste, bbls.	lb.	.14
Iodine, crude, 200-lb. kgs.	lb.	4.20
Iodine, resubl., jars	lb.	4.65
Iodoform, bot.	lb.	6.00
Iridium, metal	oz.	260.00
Kieselguhr, bags	ton	60.00
Lead, metal	lb.	.09¼
Lead acetate, bbls., white	lb.	.15
Arsenate, bbls.	lb.	.13
Oxide, litharge, bbls.	lb.	.11¾
Red, bbls.	lb.	.12¼
Peroxide, drums	lb.	.25
White, basic carb., bbls.	lb.	.10¾
Sulfate, bbls.	lb.	.10
Lime, hydrated, bbls.	100 lbs.	.85
Lime, live, chemical bbls., wks.	100 lbs.	1.05
Limestone, ground, bags, wks.	ton	4.50
Lithium carbonate, 100-lb. kgs.	lb.	1.45
Lithopone, bbls.	lb.	.06⅛
Magnesite, crude	ton	15.00
Calcined, 500-lb. bbls., wks.	ton	48.00
Magnesium, metal sticks, wks.	lb.	.85
Magnesium carbonate, bags	lb.	.06¾
Chloride, drums	ton	34.00
Fluosilicate, cryst., bbls.	lb.	.12
Oxide, U. S. P., light, bbls.	lb.	.42
Manganese chloride, casks	lb.	.06
Dioxide, 80%, bbls.	ton	80.00
Sulfate, casks	lb.	.07
Mercury bichloride, cryst., 25 lbs.	lb.	1.31
Mercury, flasks, 75 lbs.	flask	88.00
Meta-nitroaniline, bbls.	lb.	.72
Meta-phenylenediamine, bbls.	lb.	.85
Meta-toluylenediamine, bbls.	lb.	.73
Methanol, 97%, tanks	gal.	.57
Methyl acetone, drums	gal.	.83
Salicylate, cases	lb.	.43
Methyl chloride, cylinders	lb.	.50
Michler's ketone, bbls.	lb.	3.00
Monoethylaniline, drums	lb.	1.05
Naphtha, solvent, tanks	gal.	.35
Naphthalene, flake, bbls.	lb.	.06
Nickel, metal	lb.	.34
Nickel salt, single, bbls.	lb.	.08
Double, bbls.	lb.	.08½
Niter cake, bulk	ton	4.50
Nitrobenzene, drums	lb.	.09½
Oil, castor, No. 1	lb.	.14½
China wood, bbls.	lb.	.13
Coconut, Ceylon, tanks	lb.	.11
Cod, N. F., tanks	gal.	.63
Corn, crude, tanks, mills	lb.	.09¾
Cottonseed, crude, tanks	lb.	.09½
Lard, edible, bbls.	lb.	.18⅛
Linseed, bbls.	lb.	.118
Menhaden, crude, tanks	gal.	Nom.
Neat's-foot, pure, bbls.	lb.	.16¼
Oleo, No. 1, bbls.	lb.	.13½
Olive oil, denat., bbls.	gal.	1.25
Foots, bbls.	lb.	.08⅞
Palm, Lagos, bbls.	lb.	.09¼
Peanut, crude, tanks	lb.	.10
Perilla, bbls.	lb.	.15¾
Rapeseed, bbls.	gal.	.94
Red, bbls.	lb.	.11¾
Soy bean, crude, bbls.	lb.	.13¼
Sperm, 38°, bbls.	gal.	.87
Whale, bbls., natural winter	gal.	.76
Ortho-aminophenol, kegs	lb.	2.15
Ortho-anisidine, drums	lb.	2.75
Ortho-dichlorobenzene, drums	lb.	.06
Ortho-nitrochlorobenzene, drums	lb.	.32
Ortho-nitrophenol, bbls.	lb.	.90
Ortho-nitrotoluene, drums	lb.	.13
Ortho-toluidine, bbls.	lb.	.25
Palladium, metal	oz.	80.00
Para-aminophenol, kegs	lb.	1.10
Paraldehyde, tech., drums	lb.	.30
Para-formaldehyde, cases	lb.	.42½
Para-nitroaniline, drums	lb.	.53
Para-nitrochlorobenzene, drums	lb.	.25
Para-nitrophenol, bbls.	lb.	.50
Para-nitrosodimethylaniline, bbls.	lb.	.92
Para-nitrotoluene, bbls.	lb.	.25
Para-phenylenediamine, bbls.	lb.	1.20
Para-toluidine, bbls.	lb.	.50
Paris Green, 500-lb. kgs.	lb.	.19
Phenol, drums	lb.	.22
Phenolphthalein, drums	lb.	1.30
Phenylethyl alcohol, 1-lb. bot.	lb.	7.00
Phosphorus, red, cases	lb.	.68
Phosphorus trichloride, cyl.	lb.	.45
Phthalic anhydride, bbls.	lb.	.18
Platinum, metal	oz.	120.00
Potash, caustic, drums	lb.	.07½
Potassium acetate, kegs	lb.	.29
Bicarbonate, casks	lb.	.09
Bichromate, casks	lb.	.08¼
Binoxalate, bbls.	lb.	.16
Bromate, cs.	lb.	.85
Carbonate, 80–85%, calc., casks	lb.	.05¾
Chlorate, kegs	lb.	.08½
Chloride	ton	34.55
Cyanide, cases	lb.	.55
Meta-bisulfite, bbls.	lb.	.10
Permanganate, drums	lb.	.14½
Prussiate, red, casks	lb.	.37
Yellow, casks	lb.	.18
Titanium oxalate, bbls.	lb.	.30
Pyridine, drums	gal.	5.15
Quinine bisulfate, 100 oz.	oz.	.45
Sulfate, 100-oz. cans	oz.	.50
Resorcinol, tech., kegs	lb.	1.35
Rochelle salt, bbls., U. S. P.	lb.	.19
R salt, bbls.	lb.	.45
Saccharin, cans	lb.	1.75
Salt cake, bulk	ton	19.00
Saltpeter, gran., bbls.	lb.	.06¼
Silica, ref., bags	ton	18.00
Silver nitrate, 16-oz. bot.	oz.	.46⅞
Soda ash, 58%, light, bags, contract, wks.	100 lbs.	1.38
Soda, caustic, 76%, solid, drums, contract, wks.	100 lbs.	3.10
Sodium acetate, bbls.	lb.	.04½
Benzoate, bbls.	lb.	.50
Bicarbonate, bbls.	100 lbs.	2.00
Bichromate, casks	lb.	.06¼
Bisulfite, bbls.	lb.	.04
Bromide, bbls.	lb.	.48
Carbonate, sal soda, bbls.,	100 lbs.	1.30
Chlorate, kegs	lb.	.06¼
Chloride, bags	ton	12.00
Cyanide, cases	lb.	.20
Fluoride, bbls.	lb.	.08¾
Hyposulfite, reg., crys., bbls.	lb.	.02½
Metallic, drums, 12¼-lb. bricks	lb.	.27
Naphthionate, bbls.	lb.	.55
Nitrate, crude, bags, N. Y.	100 lbs.	2.55
Nitrite, bbls.	lb.	.08⅞
Perborate, bbls.	lb.	.21
Peroxide, cases	lb.	.27
Phosphate, trisod	lb.	.04
Picramate, kegs	lb.	.60
Prussiate, bbls.	lb.	.10
Silicate, drums, tanks, 40°,	100 lbs.	.75
Silicofluoride, bbls.	lb.	.04½
Stannate, drums	lb.	.42½
Sulfate, anhyd., bbls.	lb.	.02
Sulfide, cryst., bbls.	lb.	.02½
Solid, 60%	lb.	.04
Sulfocyanide, bbls.	lb.	.30
Tungstate, kegs	lb.	.80
Strontium carbonate, bbls.	lb.	.07
Nitrate, bbls.	lb.	.07½
Strychnine alkaloid, 100 oz., powd.	oz.	.61
Sulfate, powder	oz.	.42
Sulfur, bulk, mines, wks.	ton	17.00
Sulfur chloride, red, drums	lb.	.05½
Yellow, drums	lb.	.03¾
Sulfur dioxide, cyl.	lb.	.08
Sulfuryl chloride, drums	lb.	.65
Thiocarbanilide, bbls.	lb.	.24
Tin, Amer., stand.	lb.	.62
Tin bichloride, 50% sol., bbls.	lb.	.17¾
Oxide, bbls.	lb.	.64
Titanium oxide, bbls., wks.	lb.	.13
Toluene, tanks	gal.	.35
Tribromophenol, cases	lb.	1.10
Triphenylguanidine, drums	lb.	.69
Triphenyl phosphate, bbls.	lb.	.75
Tungsten	WO_3 unit	12.00
Urea, pure, cases	lb.	.18
Whiting, bags	ton	18.00
Xylene, 5°, drums, mills	gal.	.60
Xylidine, drums	lb.	.37
Zinc, metal, N. Y.	lb.	.09⅛
Zinc ammonium chloride, bbls.	lb.	.06¼
Chloride, granulated, drums	lb.	.07
Oxide, Amer., bbls.	lb.	.07⅜
Stearate, bbls.	lb.	.21½
Zinc dust, bbls., kegs, c/l.	lb.	.09