

# Industrial and Engineering Chemistry



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## A Research Program

THE Division of Cellulose Chemistry, as reported in the News Edition of November 20, has endorsed the McSweeney-McNary Bill, which is in effect an effort to authorize a ten-year program in forest research for the Department of Agriculture. The proposed legislation is thoroughly constructive and, although authorizing appropriations for various phases of forest research work, does not itself carry these appropriations.

In view of the present value of cellulose as a raw material for the chemical industry and the prospects of enhanced value in the near future, the program outlined in this bill is worthy of our careful study and support. In addition to our Division of Cellulose Chemistry, a number of scientific and commercial organizations have approved the bill. The Chamber of Commerce of the United States has issued a booklet summarizing the significant points to be covered.

While a great deal has been said and written concerning forestry, most of us do not yet appreciate the true situation. Our natural forest lands are of great extent, totaling more than 500 million acres, of which some 220 million acres are in commercial holdings; one-fifth are under federal ownership or control, chiefly in national forests; one-third in woodlots owned by farmers; and 10.5 million acres controlled by the states. As compared with research conducted in other fields, the amount expended upon forest research is small. The Society of American Foresters estimates that the current annual expenditures for forest research by all agencies probably do not exceed \$2,600,000.

This is not the place to dwell upon the necessity of producing forest crops to meet our total requirements—that is a truth accepted by all scientists. Our forests offer as great an opportunity for constructive research as did our agricultural lands when, forty years ago, the first really serious steps in agricultural research were taken. A closely printed book of some two hundred pages has been prepared, giving in detail a national program of forest research. It merits careful consideration, and it is upon this ten-year program that the bill in question is founded. The essentials fall under such main divisions as a complete and practical

science of tree-growing and protection, waste reduction in the manufacture and utilization of wood, development of economic information concerning the growing, manufacture, and distribution of wood, and the general problem of full use of the forests. Ours is the most complex temperate zone forest in the world, extending throughout our country and found on lands from sea level to 12,500 feet altitude. In our climate, which ranges from subtropical to subarctic, with precipitation varying from 20 to 140 inches a year, and with

an unknown number of soil types, we find about eight hundred and fifty widely different tree species, of which at least sixty-five are of first commercial importance. With so large a number of variables the work to be done before we really know what to prescribe in a given situation is great almost to discouragement. Even the growing of timber in the United States is in its infancy and European methods apply but roughly to our different species and conditions. Obviously, a farsighted program is needed and the American foresters have gone to great pains to prepare one.

The program provides for close coöperation with forest pathologists, forest entomologists, forest biologists, and meteorologists in the various bureaus of the federal service. There is increased work for the Forest Products Laboratory on wood utilization, and a group of problems involving the forest as a range where stock is to be pastured and game encouraged concurrently with forest development. Data on forest economics are badly needed to furnish a sound basis for the legislative and business policies of federal and state governments in encouraging forest industries, at the same time protecting the public interest.

Those who have carefully investigated the subject feel that within a decade the large program outlined will justify an annual expenditure of approximately twelve millions for research. This amount is not unreasonable for work on problems involving one-fourth of our total land area and looking to the permanence of some of our largest industries.

The program appeals to us as one which we can support, not only as chemists interested in the products of the forest, but as informed citizens who recognize without argument its importance.

### A Word from Our President

MAY I make use of the columns of INDUSTRIAL AND ENGINEERING CHEMISTRY to express to the members of the AMERICAN CHEMICAL SOCIETY my very sincere appreciation of the honor accorded me in being elected President of the SOCIETY for the current year?

Thanks to the efficiency of its past presidents and executive officers, the present status of the SOCIETY is most excellent—a circumstance which adds greatly to the pleasure of being chosen as its President. However, is this feature to be interpreted as a call to complacency, or is it a challenge?

The chemists of America in the last twenty years have been very busy and have contributed materially to science, to the industries, and to the general welfare; and withal, the SOCIETY has been well out in front of the procession functioning as helper and sponsor for every wise undertaking. It is inconceivable that the chemists of this country will now, or ever, sit down and take life easy. The present happy status, therefore, must be interpreted as a challenge. What shall it be? The year is before us.

S. W. PARR

## Chemists as Laymen

THE specialist sometimes wonders how certain elementary discussions can find a place in the crowded journals of the day, but he forgets that what is elementary to him may not be so elementary to many of his fellow workers. One of the ideas upon which the Institute of Chemistry of the AMERICAN CHEMICAL SOCIETY is based is that chemistry in many of its ramifications must be interpreted to other chemists almost as much as to the intelligent layman. When the specialist in one line speaks to specialists in other lines, he frequently finds it necessary to make his explanation as simple as possible. The man whose classroom days belonged to an earlier generation must be served and to some of these successful men the new chemistry is something of a new science.

So when you find in the columns of this and other technical journals material which seems of small importance to you, remember there are others who may not have had your experience or background but who nevertheless are sufficiently interested in your subject to wish new information, if it can be quickly and easily assimilated.

## Paper in Agriculture

WHEN the manager of a sugar plantation in Hawaii decided to fight weeds by covering the field with a heavy waterproof paper through which the bayonet-like tips of the growing cane would penetrate and, when later, a similar paper was spread with great gain between rows of pineapple, little thought was given to the application of this process to American agriculture. In a recent meeting, however, a member of the Department of Agriculture reported results from various garden crops which may be full of significance. Following three years of research, it was found that all but one of the ordinary garden crops responded with a heavily increased yield when all unoccupied soil spaces were covered with the paper. During the 1927 season results varied from 11 per cent with garden peas to 516 per cent with spinach, between which extremes the crop of lettuce more than doubled, green corn trebled, and potatoes almost quadrupled. The paper serves to increase the soil temperature, reduces the loss of moisture, smothers weed growth, and modifies the distribution of water.

On such an experimental scale it was difficult to obtain all the economic factors which must be known before paper-mulching on a large scale can be recommended to truck gardeners and farmers. It does not seem impossible, however, that the use of such paper may contribute greatly toward increased production on fewer acres—one way of assisting agriculture through decreasing costs by the simple method of increasing returns per unit of labor and land employed.

## Endowed Association Research

OUR belief in the efficacy of research conducted by trade associations as a defensive and, indeed, offensive weapon in the new competition has frequently been voiced. Just as there is a variance in the research of individual industries, so there are various kinds and degrees of trade association research. On the whole it has been satisfactory and encouraging. At times it has almost failed for a variety of causes, such as internal politics, the unfortunate choice either of director or of problems, or the lack of appreciation on the part of the membership that the time factor always looms large in a research program.

The wise industry engaged coöperatively upon research, service, and development work eliminates as many of these difficulties as possible. The inability of certain members of a group to apply at once to their own problems the data secured in the laboratory sometimes leads to discouragement and the withdrawal of support. Even the best managed and directed laboratory may approach financial starvation in times of economic stress. The endowment for the research laboratory of an association gives at once a permanence which, in itself, renders ineffective causes which might otherwise wreck the whole program.

We have long been interested in the determination of the Tanners' Council of the United States of America to introduce into their industry the services of science, potentially great and already valued by many individual producers of leather. A few years ago a research laboratory was established at the University of Cincinnati, and the results achieved seem to the leaders of the industry of such fundamental value as to make them determined to put the laboratory upon a permanent foundation, independent of trade fluctuations and, indeed, of the life of the association itself. The laboratory has consequently become incorporated and a group of manufacturers is engaged in raising an endowment, the income of which will be devoted to research.

There are many ways of supporting trade association research, each perhaps best suited to the industry represented, but where security is desired the independent establishment of the laboratory upon an adequate foundation seems to offer the best answer.

## Funds for Textile Research

NEWS comes to us that the principal difficulties in the way of utilizing funds belonging to the Textile Alliance, Inc., have disappeared and that only a few unimportant questions between the Alliance and the Government remain to be settled. It may be remembered that the Textile Alliance, Inc., acted as a quasi-governmental agency in the importation of dyes and other essential products for the textile trade after the United States entered the war. In the course of its dyestuff operations a fund of nearly two million dollars was accumulated which, under an agreement with the State Department, was to be devoted to scientific research and education. Later some difficulties arose in the course of which the Treasury Department laid claim to about one and a quarter millions of the fund under the income tax and excess profits tax law. A recent decision annuls this tax claim and now, after the loss of a number of years during which the income from this fund might have been helping the textile industry through research, attention must soon be given to this important question.

Several years have passed since we actively endeavored to interest those responsible for the use of the fund as a nucleus for a textile research institute. At that time some of the officials of the Alliance were inclined to think that the fund should be allocated in different states, somewhat in proportion to the underwriting which the members of the Alliance had supplied and which they had never been called upon to pay. There are doubtless many who still feel that the way to derive the greatest benefit from this fund for the industry which really created it would be to devote it to existing research problems.

We differ strongly with this feeling, for we are convinced that notwithstanding the effect of recent depression in the textile trade, awakening its leaders to the potentialities of science, there is still no prospect of the industry itself setting up such an institute as it sorely needs unless some such

substantial nucleus can be created. We do not mean that it is necessary at once to build a new laboratory and equip it, but we do mean that this fund should be kept intact, and that the income from it should be used for such pressing problems as now present themselves. There should be no continuing appropriations, for no one can foresee just which problem is going to be the important one tomorrow. The fund will support a limited amount of work, but if properly managed the results should at once attract additional sums from the industry, and with such a beginning a textile research institute can gradually be expanded to the point where it can undertake the important research on the many diverse problems which confront the producers and users of the several fibers employed. To scatter the fund means to waste it. To use it for the endowment of a textile research institute means that our own textile industry will finally engage upon research on a scale somewhat comparable to that already achieved in Great Britain and initiated in some of the other countries.

## Is Success to Be Penalized?

IT IS a common observation that those who have never sought assistance and have been successful without special aid have greater difficulty in securing help when it is needed than those who have been more or less dependent on others. The man who habitually pays cash and discounts his bills has more trouble in getting credit, if needed, than those who are experienced in borrowing money and dodging bill collectors. We should not be surprised, therefore, to find some incredulous when told that if certain activities of the AMERICAN CHEMICAL SOCIETY are to be maintained and developed on an adequate scale to meet present conditions, there must be money beyond present resources. As is well known, the record of the SOCIETY in developing a publication program to carry out its objects as laid down in the Constitution is unique. One needs but to compare the value, as measured by worthy publications supplied to members of various societies, to realize how great has been our SOCIETY'S success, achieved without a great amount of assistance. We have on record but a few special grants to aid in times of particular stress or to restore to our capital funds amounts needed to continue publication under unusual circumstances. American chemists have been more fortunate than many of their fellow scientists in having laid down for them the broad principle that, whatever their diversification and special interests, they should unite in the work of promoting the science. The men foremost in applied chemistry and those responsible for the advance of fundamental work have always joined forces in the furtherance of our work. The data show how well the affairs of the SOCIETY have been managed, and while there may be differences of opinion as to the proportion of the SOCIETY'S income that should be expended for certain types of development, the actual financial management has always been in strong hands. As the need has arisen, new projects have been courageously launched and carried to a satisfactory point of service.

A failure to recognize the soundness of these principles has given rise to the existence of several small groups of specialists, each too small to develop adequate publication facilities without external aid. It is only recently that representatives of one great science have united for a publication project. The process required the utmost tact over several years, being finally completed with the aid of a substantial grant from one of the great philanthropic foundations.

Our very success now appears a handicap in securing much needed assistance. It is hard for certain sources of funds to realize that not only has chemistry advanced at a much

greater rate than the financial resources of the AMERICAN CHEMICAL SOCIETY, but that the numerous fellowships, institutes, and new research centers created by individuals and philanthropic foundations have resulted in an increase in the papers to be printed and abstracted. This has actually imposed a further burden of fair proportions upon the SOCIETY, welcome though it is. The chemical industry is pointed out as the benefactor of all this work, and the SOCIETY is invited to turn to it, even though many members of this industry have so recently become established in production as to make it difficult for them to support publication on the basis which they recognize as desirable.

The fundamental character of chemical work indicates how extensive should be the assistance given our program. Today medicine looks to chemistry more than to any other one science for the coöperation which will advance the work of preventing and curing disease. Structural materials, as we well know, depend for their perfection upon research as well as chemical control. In a number of directions progress in such major divisions of human activity as transportation, communication, food production and preservation wait upon new discoveries in the chemical laboratory. We would not be misunderstood as claiming for chemistry the riches of the world, but there can be no disagreement as to the necessity of those contributions which chemistry has made, and is yet to make, to the work of so altering materials of Nature as to render them more satisfactory for man's needs. In many cases it becomes our duty to explain to industry, which strictly speaking may not be classified as chemical, the utility of the chemical literature to all and sundry and the special value of our key to articles in all languages. In fine, *Chemical Abstracts* presents a rare opportunity to reap the profits that come from well-managed coöperative buying, since no one with many, many times the present expenditure could do for himself what *Chemical Abstracts* does for all.

In laboratories everywhere *Chemical Abstracts* is looked upon as one of the most useful tools. It is felt that this tool can continue to be satisfactory only if the policy of completeness can be maintained and recognized weaknesses, which inadequate funds have caused, can be removed. In an effort to maintain the proper standard, the Directors have continually increased the appropriation for *Chemical Abstracts*. In 1907, \$17,450 was appropriated. The minutes of the last meeting show a regular appropriation of \$110,000 for 1928, with a supplementary sum of \$12,700 to be placed at the disposal of the editor of *Chemical Abstracts*, even if it becomes necessary to take this sum from invested funds. The Directors explain that "This was done for the reason that it was felt that the present policy of abstracting all chemical articles appearing in the world should be continued for at least one more year before changing the policy of the SOCIETY, in the hope that in the interim funds might become available to continue *Chemical Abstracts* on a scale warranted by its unquestioned importance in both pure and applied chemistry."

Those responsible for the SOCIETY'S finances are making careful plans in the hope that an adequate capital sum may be secured to guarantee the future of *Chemical Abstracts*. It is a matter for them to plan, but the members of the SOCIETY will doubtless be called upon to assist in one way or another in carrying out whatever is decided. There is no question but that the value of *Chemical Abstracts* should be maintained at the highest possible level. Ample organization for the enterprise has become established. The editorial work is in capable hands and members everywhere coöperate. Our pressing problem is that of finding the necessary funds which will have to come from sources other than those now available.

# Development of Synthetic Phenol from Benzene Halides<sup>1</sup>

William J. Hale and Edgar C. Britton

ORGANIC RESEARCH LABORATORY, THE DOW CHEMICAL COMPANY, MIDLAND, MICH.

IN THOSE early days when Kékulé (1865) first announced his ring formula for benzene, the organic chemists were steadily at work endeavoring to aid in this interpretation through a study of replacements among benzene substituents. Thus the replacement in benzene of halogen by the hydroxyl group occupied the attention of many of our early investigators. The comparative resistance to chemical action as displayed by benzene halides only contributed to the zest for such accomplishment and, as might be expected in the handling of a more or less refractory material, the early records could not escape the introduction of numerous inconsistencies.

Laurent and Gerhardt<sup>2</sup> reported the preparation of chlorobenzene by the action of phosphorus pentachloride on phenol and, furthermore, the hydrolysis of this chlorobenzene into phenol when heated with aqueous caustic potash. Again, Church<sup>3</sup> reported the action of alcoholic potash upon chlorobenzene as leading to a reaction mass which could be made to yield phenol on acidification. Temperature and pressure were not mentioned. In both these references we have evidently to consider the employment of an impure chlorobenzene, as evidenced by the work of Riche,<sup>4</sup> who heated a mixture of carefully purified chlorobenzene and alcoholic potash for 15 hours in a sealed tube (at boiling temperatures) and obtained no apparent indication of hydrolysis; and further as evidenced by the work of Fittig,<sup>5</sup> who first attempted to bring about the decomposition of bromobenzene by the action of silver acetate and by alcoholic potassium acetate in sealed tubes, but with negative results even after a week of heating. Later, Fittig<sup>6</sup> verified the results of Riche.<sup>4</sup>

The first actual accomplishment of the hydrolysis of chlorobenzene was reported by Dusart and Bardy<sup>7</sup> where only brief mention is made of heating chlorobenzene and caustic soda in aqueous solution to 300° C. in closed vessels and isolating phenol from the reaction product. This result, as commented upon by Henninger,<sup>8</sup> was not generally accepted; at least no particular interest was aroused and the research lay untouched for many years.

Fritz Blau,<sup>9</sup> conceding that no real success had as yet been attained in the replacement of halogen by hydroxyl among benzene substituents, essayed to accomplish this replacement of halogen by methoxyl. He heated bromobenzene with sodium methylate in a sealed tube for 24 hours,

at 230° C. and sometimes as high as 270° C. The reaction proceeded only slowly. The reaction product was found to contain not anisol alone but considerable phenol and diphenyl oxide, the sum total indicating a 40 per cent conversion of the original bromobenzene.

The use of copper as a catalytic agent for the splitting off of halogen from its position as substituent in the benzene molecule was first announced by Ullmann in 1900. Ullmann and Sponagel<sup>10</sup> thus proved the order of retention of chlorine, bromine, and iodine by the aromatic nuclei decreased with an increase in the atomic weights, respectively, of the substituents. It was found later<sup>11</sup> that in the replacement of these halogen substituents a stepping-up in the quantity of copper catalyst employed contributed in corresponding ratio to speeding up the reaction. A large number of reagents for aromatic halides were brought under investigation in the presence of copper. In the use of ammonia for reaction with the aromatic halides, it was necessary to bring the aqueous solution into contact with the halides under pressure.

In a patent granted to the Aktien Gesellschaft<sup>12</sup> it is distinctly stated that copper salts are serviceable in aiding the removal of halogens from aromatic halides for reaction with aqueous ammonia. Thus chlorobenzene, when heated under pressure with an excess of aqueous ammonia and copper sulfate at 180–200° C. for 20 hours, actually gave a yield of 80 per cent in aniline.

The distinct advantage of metallic copper in aiding the hydrolysis of halogen derivatives of benzene was evidenced in a patent to F. Bayer,<sup>13</sup> in which the hydrolysis of halogenated phenols by aqueous solutions of alkaline-earth hydroxides, with or without the addition of alkali hydroxides, was carried out in closed copper vessels heated to 170–200° C. under pressure and with stirring. In this patent mention is made of the use of alkali iodide as catalyst, the principle underlying its use having been previously observed by Wohl<sup>14</sup> in connection with the replacement of a chloro group in organic molecules by an iodo group and then by a cyano group as leading to better yields than where no intermediary substitution by iodo group was made.

Shortly afterward Torley and Matter were granted British and French patents<sup>15,16</sup> for the preparation of polyhydric phenols from *o*- and *p*-dichlorobenzenes by the action of caustic alkali in 15 per cent aqueous solution, under pressure, at 300–350° C., and in the presence of metallic copper. These investigators were granted further patents<sup>17,18</sup> for

In this article is set forth the history and development of the hydrolysis of benzene halides. The writings of organic chemists have never fully acknowledged the practicability of such procedure when applied to the simple process of producing phenol from halogenated benzene. It is now demonstrated that synthetic phenol can be made commercially from halogenated benzene and at a price appreciably lower than by any other process.

<sup>1</sup> Presented by W. J. Hale before the Division of Dye Chemistry at the 74th Meeting of the American Chemical Society, Detroit, Mich., September 10 to 15, 1927.

<sup>2</sup> *Compt. rend.*, **28**, 170 (1849); *Pharm. Zentralblatt*, **1849**, 314.

<sup>3</sup> *J. Chem. Soc. (London)*, **1**, 76 (1863); *Ann.*, **128**, 216 (1863).

<sup>4</sup> *Ann.*, **130**, 256 (1864).

<sup>5</sup> *Ibid.*, **121**, 363 (1862).

<sup>6</sup> *Ibid.*, **133**, 49 (1865).

<sup>7</sup> *Compt. rend.*, **74**, 1051 (1872).

<sup>8</sup> *Ber.*, **5**, 389 (1872).

<sup>9</sup> *Monatsh.*, **7**, 626 (1886).

<sup>10</sup> *Ann.*, **350**, 83 (1906).

<sup>11</sup> *Ibid.*, **355**, 316 (1907).

<sup>12</sup> D. R. P. 204,951 (1908).

<sup>13</sup> D. R. P. 249,939 (1912).

<sup>14</sup> *Ber.*, **39**, 1951 (1906).

<sup>15</sup> British Patent 9450 (April 22, 1913).

<sup>16</sup> French Patent 458,136 (April 23, 1913).

<sup>17</sup> British Patent 9451 (April 22, 1913).

<sup>18</sup> French Patent 457,843 (April 23, 1913).

the preparation of phenyl ether by the action of alkali alcoholates or phenates upon halogenated aromatic hydrocarbons at 320° C. and in the presence of copper as catalyst. The effectiveness of temperatures higher than 300° C. was made apparent in these two patents. As regards the use of metallic copper in this connection, we may quote from the patent specifications embodied in the first British Patent:<sup>18</sup> "The activity of such catalytic or contact substances depends upon the surfaces exposed and upon the character of the surfaces."

The use of methyl alcohol, either anhydrous or admixed with water, as a solvent for the various alkali hydroxides, in their employment as hydrolytic agents upon benzene halides, was announced by Ichendorf.<sup>19</sup> A temperature of 200–230° C. for 45 hours sufficed for a 90 per cent yield in phenol from chlorobenzene, by this procedure, and a temperature of only 190° C. for 40 hours sufficed for an 80 per cent yield in *o*-chlorophenol from *o*-dichlorobenzene.

At the same time Meyer and Bergius (the latter now of Bergin process fame) were at work in Hanover upon a study of hydrolytic agents at higher temperatures on benzene halides. They applied for patents to cover some of the practical features. A U. S. patent<sup>20</sup> was granted to them on a process for heating, under pressure, chlorobenzene or  $\alpha$ -chloronaphthalene with caustic alkali in 10 per cent aqueous solution at a temperature of 300° C. The application for a patent in Germany remained only as an Anmeldung M. 53,721.<sup>21</sup>

The researches of Meyer and Bergius<sup>22</sup> as published constituted the most exhaustive presentation of hydrolytic studies upon chlorobenzene that had as yet appeared. The tendency of chlorobenzene and caustic alkali mixtures to tar formation at temperatures around 300° C. drove these investigators to the use of dilute caustic alkali solutions. Water alone upon chlorobenzene at 300° C. was found to give only a trace of phenol. Equimolecular proportions of chlorobenzene and caustic alkali did not effect more than a 70 per cent hydrolysis, with the quantity of diphenyl oxide almost equal to that of phenol in the final product; but in the presence of 2 mols of caustic alkali to 1 of chlorobenzene they were able to obtain almost complete hydrolysis, or conversion, and a product consisting of about 2 parts phenol to 1 of diphenyl oxide.

Again, when 1 mol of chlorobenzene was mixed with 4 mols of caustic alkali (in 15 per cent aqueous solution) and heated for 20 hours in a stationary bomb at 300° C., these chemists obtained a 92 per cent yield in phenol. The long reaction time contributed to a less amount of diphenyl oxide in the reaction product. This was interpreted, and correctly so, as due to the action of excess of alkali at higher temperatures upon the diphenyl oxide intermediately formed. Five mols of caustic soda under the same conditions as above led to a 94 per cent yield in phenol and no diphenyl oxide. When a proportion of 2½ mols of caustic alkali to 1 mol of chlorobenzene was employed, it was necessary to extend the reaction time to 26 hours, in rotating autoclaves, in order to secure the optimum conversion and a yield of 90.8 per cent in phenol and 4.7 per cent in diphenyl oxide. The residue, 4.5 per cent, consisted of tar.

In order to ascertain what effect the presence of a catalyst might have upon the hydrolysis of benzene halides under pressure, Meyer and Bergius added cupric chloride to a reaction mixture of 1 mol chlorobenzene and 2¼ mols caustic soda in dilute aqueous solution, and heated the mixture in a rotating autoclave to 200° C. for 8 hours. A yield of

3.77 per cent phenol was obtained. Under these same conditions, without a catalyst, they were able to detect little or no hydrolytic action on the chlorobenzene. When the hydrolysis of chlorobenzene was conducted at 300° C. in the presence of a catalyst, these investigators reported that in a rotating autoclave 1 mol of chlorobenzene, 2 mols of caustic soda (of 15 per cent concentration) and ⅓ mol of cupric chloride, heated for 2 hours, resulted in complete hydrolysis, with a yield of 84.6 per cent phenol and 8.2 per cent diphenyl oxide; the residue of 6.4 per cent was, of course, tar.

Though the copper salt speeded up the reaction, it also increased the tar formation. Bromobenzene and  $\alpha$ -chloronaphthalene were likewise submitted to the action of caustic soda in aqueous solution; the last-named required a much longer reaction time and a temperature above 300° C. for complete hydrolysis.

Meyer and Bergius extended their investigations upon chlorobenzene to include the hydrolytic action of cases other than caustic soda. The results obtained by them are of such general interest that they are here reproduced (Table I). No catalysts were employed in this set of experiments. In a rotating autoclave chlorobenzene was made to react with aqueous solutions of the substances indicated.

Table I—Hydrolytic Action of Bases (Meyer and Bergius)

BASIC SUBSTANCE	TEMPERATURE ° C.	TIME Hours	YIELD, PER CENT OF THEORETICAL		
			Chlorobenzene	Phenol	Diphenyl oxide
Milk of lime	300	9	84	Trace	..
Milk of lime	330	9	81	..	..
Sodium carbonate	300	8	64	15	..
Sodium carbonate	305	8	..	34.6	13.7
Borax	297	9	44	15	..
Ammonia solution	300	8	30% aniline	7	10

In this same year and the succeeding year we note a number of patents taken out by Boehringer and Soehne,<sup>23 to 26</sup> in further application of these catalytic studies:

(1) The use of aqueous solutions of alkali carbonates, as well as alkali hydroxides, and mixtures of the same, upon chlorophenols, in the presence of metallic copper and also copper salts in silver bombs, under pressure.<sup>23</sup> For example, *o*-chlorophenol heated for 9 hours under such conditions at 190° C. gave a yield of 83.5 per cent in pyrocatechol.

(2) The partial hydrolysis of dihalogen-substituted benzenes into halogenated phenols by the use of aqueous and aqueous-alcoholic solutions of alkali hydroxides or carbonates, under pressure, and in presence of copper or copper salts.<sup>24</sup>

(3) The use of aqueous alcoholic solutions of alkaline-earth hydroxides mixed with alkali hydroxides, for reaction upon dihalogen-substituted benzenes in copper vessels, under pressure, and with addition of potassium iodide as a further catalyst, particularly in reactions employing *o*-dichlorobenzene.<sup>25</sup>

(4) Applies the principles mentioned above to the instance of chlorobenzene and its hydrolysis into phenol, making use therefore of an aqueous solution of alkali and alkaline-earth hydroxide mixtures in presence of potassium iodide, and in copper vessels, under pressure, at 240–250° C. for 40 hours. A 70 per cent yield in phenol is reported.<sup>26</sup>

Several years subsequent to the researches of Meyer and Bergius there was granted to Aylsworth, in this country, a patent<sup>27</sup> in which was set forth a new procedure for effecting organic chemical reactions at high temperatures and pressures and in a continuous system. Chlorobenzene, as well as benzenesulfonic acid, was here brought into action with fairly strong caustic alkali solutions for production of alkali phenate and, in turn, phenol. The temperature recommended was 340–390° C., or approximately that range cover-

<sup>18</sup> D. R. P. 281,175 (1914).

<sup>19</sup> U. S. Patent 1,062,351 (May 20, 1913).

<sup>20</sup> Friedlaender, XII, 160.

<sup>21</sup> Ber., 47, 3155 (1914).

<sup>22</sup> D. R. P. 269,544 (1914).

<sup>23</sup> D. R. P. 284,533 (1915).

<sup>24</sup> D. R. P. 286,266 (1915).

<sup>25</sup> D. R. P. 288,116 (1915).

<sup>26</sup> U. S. Patent 1,213,142 (1917).

ing the critical temperatures of water (372° C.) and chlorobenzene (362° C.). The pressure was to be always slightly in excess of that pressure represented by the tension of aqueous vapor at the temperature of operation (from 2000 to 4000 pounds per square inch, as stated in the patent). At such high temperatures the hydrolysis of benzene derivatives proved to be complete in one hour or less.

The most distinguishing feature of the Aylsworth process lies in the use of a continuous-system, or tubular, autoclave. It was not to be supposed that the ordinary type of autoclave could be constructed to withstand such high pressures as here stipulated, without undue expense and considerable difficulty in the way of heat supply. There was, however, every likelihood of success in attaining these high pressures, as well as temperatures, by employment of extra heavy iron tubing; pipe of 0.5 to 1 inch inside diameter and 1.5 to 2.5 inches outside diameter constituting marketable material. Naturally, the process required the installation of efficient and powerful pumps to force the feed liquor through the coils of tubing. Furthermore, in any continuous system under high pressure there must be devised some means of withdrawing the reaction products without materially changing the pressure in the reaction system. To this end Aylsworth employed an accumulator, or hydraulic-pressure regulator, on the further end of the tubular set-up. The weight of the accumulator was allowed to rest upon a piston moving within a heavy pipe which was connected at its base with the tubular system. Thus, by balancing this weight of accumulator against the pump pressure the pressure on the exit needle valve in the system was held constant against variations in rates of pumping and release.

According to Aylsworth's plan, the coils of steel tubing were held immersed in huge sodium nitrite baths. Heat supplied to these baths was transmitted readily and evenly through the molten nitrite to the steel tubing and, as distinctly pointed out in the patent specification, the necessity for even heating cannot be exaggerated.

In order to insure a better mixing of reaction components as well as a speedier supply of heat to same, Aylsworth introduced a second set of pumps near the further end of the system and with such adjustment that when in operation they would be able to pump a fractional portion of the hot reaction liquor from the tubing at the further end of heated zone and return same to the forward end of this same tubular system just prior to its entrance into heated zone.

In general, 2¼ mols of caustic soda in 18 to 30 per cent aqueous solution were employed for each mol of chlorobenzene. It is, however, to be recorded that neither in the patent proper nor in the British patent to Aylsworth,<sup>28</sup> nor in a description of the process as given by Brown,<sup>29</sup> is any mention made of the yield in phenol, diphenyl oxide, and other by-products obtained in this process. There is no record of the installation of this process upon a large scale, hence we may assume that whatever success attended its early installation on a small scale must have been overshadowed by unforeseen difficulties later encountered.

In this country also, and at approximately the same time, Herbert H. Dow took up the investigation of the hydrolysis of bromobenzene.<sup>30</sup> An aqueous caustic soda solution is here shown to be effective in the hydrolysis of bromobenzene and at as low a temperature as 250° C., with a yield of phenol amounting to 85 per cent.

In 1920 Rosenmund and Harms<sup>31</sup> reported the action of several salts of strong bases and weak acids upon benzene halides. Bromobenzene was brought together with an

aqueous alcoholic solution of sodium acetate, together with a little calcium carbonate and copper acetate, and heated under pressure at 240° C. for 15 hours, and finally at 280° C. for 5 hours. The reaction product, extracted with ether, yielded a halogen-free, oily product. The aqueous residue, upon acidification, gave a yield of 50 per cent in phenol. Borax in place of sodium acetate resulted in an aqueous solution which, upon acidification, liberated only a 25 per cent yield in phenol.

During the World War enormous quantities of phenol were manufactured by the benzenesulfonic acid-sodium hydroxide fusion process. At the close of the war all countries were left with enormous stocks of phenol on hand. In 1920 our own Government had in its possession some 15 million pounds of phenol for immediate disposal. A price of 12 cents per pound was fixed and a period of five years estimated as limit of time for disposal at such price. By the fall of 1922 all of this phenol had been sold. This was a clear indication that phenol must again be synthesized in this country; and even though the sulfonation-fusion process had shown itself to be thoroughly practical, nevertheless it was the duty of chemists to strike out along new lines. Furthermore, most of the organizations which had employed the old process during the war had already scrapped their phenol plants.

#### Laboratory Investigations

Up to 1922 the state of knowledge as regards the hydrolysis of benzene halides left much to be desired, if such development were ever to be applied commercially. The interesting results reported with bromobenzene gave some hope of commercial application, and thus it was that this laboratory undertook anew the study of phenol production from benzene halides.

APPARATUS—In June, 1922, we placed in operation a type of rotating bomb of 400 cc. capacity, with fins projecting from its interior walls such as would make for a fair degree of mixing of the contents. These bombs were made of heavy pipe (iron, copper, and other materials). Two longitudinal baffles were welded into the pipe; the butt end of the pipe was then welded to a plug carrying a bearing surface outermost, and the other end was welded to a smaller pipe, in turn provided at its further end with beveled surface, upon which a closely-fitting cap was placed and made secure in such position by a union covering both cap and smaller pipe. An ordinary sprocket wheel fitted to a split coupling was placed on the near end of narrow pipe and by means of chain drive over this wheel the entire bomb was rotated.

PROCEDURE—After considerable study of heat transfer through the walls of these bombs, we adopted the procedure of heating up the sodium nitrite bath to a temperature 50° C. higher than that at which the run was to be made, and then inserting the cold bomb, two-thirds filled with reaction components. Additional experiments proved that under such conditions the contents of the bomb would reach the desired temperature and the bath drop to the desired temperature in from 5 to 10 minutes (depending upon particular bomb used), after which the initial time was taken and the bath and bomb continued under uniform electrical heating. The final temperature inside the bomb never varied more than 4° C. from the bath temperature. Consideration of conditions underlying the exothermal reactions at hand brought our timing of the runs even closer than ordinarily to be expected.

At the end of the time allotted for reaction the bombs were withdrawn from this hot bath and immediately plunged into cold water. Each bomb was then opened and the contents were removed by careful washing. The empty bomb was then further washed with acetone and alcohol and finally

<sup>28</sup> British Patent 103,664 (December 20, 1917).

<sup>29</sup> *Ind. Eng. Chem.*, **12**, 279 (1920).

<sup>30</sup> U. S. Patent 1,274,394 (1918).

<sup>31</sup> *Ber.*, **53**, 2226 (1920).

steamed and dried preparatory to further use. The reaction contents of the bomb were first submitted to steam distillation for removal of diphenyl oxide and unacted-upon benzene halides. The aqueous residue was divided into aliquot portions, one of which was titrated for phenol with potassium bromate plus bromide solution in presence of hydrochloric acid, and another portion titrated for total halogen by the Volhard method to determine percentage conversion.

**EFFECT OF ALKALI CONCENTRATION**—A careful study of all the earlier work in this domain showed conclusively that a highly concentrated caustic alkali solution led more quickly to complete conversion of the aromatic halide but invariably to larger production of tar. On the other hand, a highly diluted caustic favored particularly the formation of diphenyl oxide in place of phenol. Our first experiments (Table II) consisted

primarily, therefore, in determining the proper concentration of caustic soda upon which to base our studies. From Table II it is clear that at higher concentrations of caustic soda we meet with greater differences between percentage yield in phenol and the total hydrolysis, as based upon the chlorobenzene used. This difference is representative of the tar and other by-products of the reaction. At so low a concentration as 3 per cent comparative results required a higher temperature, but clearly demonstrated a lesser formation of undesired material. At concentrations over 11–12 per cent we were confronted with extremely high formation of undesired material. Our experiments in general pointed to an optimum concentration in caustic soda as lying between 6 and 10 per cent. The medium, or 8 per cent, was adopted as the standard. Discussions later will point in favor of a lower figure, but for the usual bomb experiments our choice proved thoroughly practical.

Table II—Effect of Concentration of Caustic Soda (Rotating iron bomb)

C <sub>6</sub> H <sub>5</sub> Cl	NaOH	H <sub>2</sub> O	CONCN.		TEMPERATURE	PHENOL	CONVERSION
			AQ. SOLN.	%			
Grams	Grams	Mols	Cc.	%	° C.	Hour	%
30	25.1	2 1/4	135	15.6	340	1	59.5
30	25.1	2 1/4	209	10.7	340	1	59.0
21.5	18	2 1/4	207	8	340	1	66.0
14.6	13.4	2 1/2	247	5	370	1	80.0
9	8.3	2 1/2	250	3	370	1	82.0

**HYDROGEN FORMATION**—There is no record in the early studies of the building up of tar when metal bombs were used. The tendency for hydrogen formation under just these conditions must have led to more and more of the hydrogenated aromatic derivatives the longer the reactions were run. It is these hydrogenated derivatives that particularly contribute to tar production. In our blank experiments with caustic soda alone and of high concentration in iron bombs, at these high temperatures, we noted the production of considerable hydrogen and the incrusting of the bomb walls with a mat of magnetic iron oxide. This tendency to hydrogen formation is apparent even with an 8 per cent caustic solution when heated in contact with iron at 300° C., but its continued formation is materially reduced in the bombs by reason of the protection which the iron oxide lining affords the interior surface of the bomb. Copper, on the other hand, does not react so readily with hot caustic, but when this caustic passes

15 per cent in concentration and is brought into contact with a copper bomb at about 350° C., a considerable amount of hydrogen is evolved. Even nickel, in still more highly concentrated caustic and at a temperature of about 350° C., will be found to replace appreciable quantities of hydrogen.

**EFFECT OF TEMPERATURE**—Some of the first experiments involving hydrolysis of bromobenzene and chlorobenzene, with increasing temperatures, are given in Table III. From the results given for chlorobenzene we may construct the time-temperature curve (curve I, Figure 1), starting with values obtained at 295° C.; the yield in phenol over this high temperature range may be considered constant at 90–92 per cent.

Table III—Effect of Temperature on Hydrolysis of Bromobenzene and Chlorobenzene (In rotating iron bomb)

CATALYST	C <sub>6</sub> H <sub>5</sub> Br	NaOH	CONCN.		TEMPERATURE	TIME	YIELD
			AQ. SOLN.	%			
(1/20 mol)	Grams	Mols	%	° C.	Hours	%	C <sub>6</sub> H <sub>5</sub> OH
BROMOBENZENE							
None	30	2 1/2	8	236	2 1/2		89
None	30	2 1/2	8	265	3/4		93
None	30	2 1/2	8	280	1/2		99
0.8	30	2 1/2	8	220	6		56
CHLOROBENZENE							
0.8	21.5	2 1/2	8	220	6 1/2		1.5
0.8	21.5	2 1/2	8	255	6		45.5
0.8	21.5	2 1/2	8	282	4 1/2		84
0.8	21.5	2 1/2	8	295	3		90
0.8	21.5	2 1/2	8	316	1		92
0.8	21.5	2 1/2	8	335	1/2		92
0.8	21.5	2 1/2	8	370	1/6		91.5

From results in Table IV we may construct the time-reaction curve II for operations at 316° C.—i. e., 1500 pounds pressure per square inch—in presence of a catalyst; and again, the corresponding time-reaction curve III for operations at 370° C.—i. e., 3000 pounds per square inch—in the absence of a catalyst. These widely varying temperatures are brought into closer relation through the action of catalyst. (Figure 2)

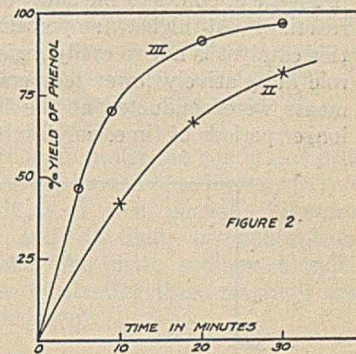


Table IV—Hydrolysis at 316° and 370° C. (In rotating iron bomb)

CATALYST	C <sub>6</sub> H <sub>5</sub> Cl	NaOH	CONCN.		TEMPERATURE	TIME	YIELD
			AQ. SOLN.	%			
(1/20 mol)	Grams	Mols	%	° C.	Min.	%	C <sub>6</sub> H <sub>5</sub> OH
0.8	21.5	2 1/2	8	316	30		82
0.8	21.5	2 1/2	8	316	19		67
0.8	21.5	2 1/2	8	316	10		42
None	21.5	2 1/2	8	370	30		97
None	21.5	2 1/2	8	370	20		92
None	21.5	2 1/2	8	370	9		70
None	21.5	2 1/2	8	370	5		47

If we substitute in the formula for unimolecular reaction

$$K = \frac{1}{t} \log_e \frac{A}{A - X}$$

where  $A$  = quantity of chlorobenzene used  
 $X$  = quantity of phenol produced  
 $t$  = time in minutes

the values given in Table IV at both 316° and 370° C., we obtain a constant— $K = 0.0095$  to  $0.0098$ . If we substitute these same values in the formula for a bimolecular reaction, we obtain no constant. We have therefore to consider the reaction under study as one of simple hydrolysis of chlorobenzene by water—an exact parallel to the hydrolysis of ethyl acetate by water. Our inability to speed up these hydrolytic reactions by increasing the concentration of the

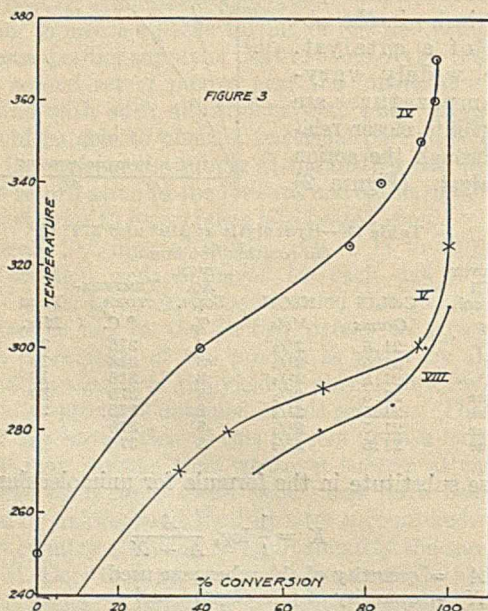
caustic alkali is proof itself of the unimolecular nature of such reactions.

**EFFECT OF CATALYST**—The hydrolysis of chlorobenzene as carried out in steel and copper bombs is given in Table V.

Table V—Hydrolysis of Chlorobenzene in Steel and Copper Bombs

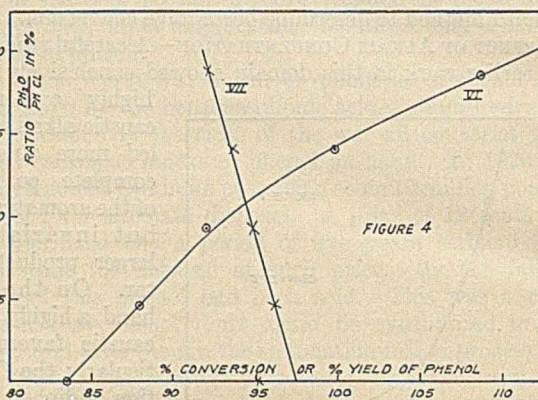
C <sub>6</sub> H <sub>5</sub> Cl Grams	NaOH (2 1/4 mols) Grams	WATER Cc.	CONCN. AQ. SOLN.		TEMPERA- TURE ° C.	TIME Hour	PHENOL %	CON- VERSION %
			%	%				
ROTATING STEEL BOMB								
18.6	15	130	10	250	1	0	0	
39.8	31	270	10	300	1	27.2	39.3	
21.5	18	207	8	300	1	41.0	48.7	
21.5	18	207	8	325	1	60.0	76.5	
21.5	18	207	8	340	1	66.3	83.7	
21.5	18	207	8	350	1	75.2	93.8	
21.5	18	207	8	360	1	77.9	96.8	
21.5	18	207	8	370	1	79.0	96.3	
ROTATING COPPER BOMB								
18.6	15	130	10	250	2	10.0	11.0	
18.6	15	130	10	250	4 1/4	57.7	58.5	
18.6	15	130	10	250	8	66.8	67.7	
18.6	15	130	10	270	1 1/2	7.8	7.9	
18.6	15	130	10	270	1	34.5	34.8	
18.6	15	130	10	270	2 1/2	68.2	70.7	
18.6	15	130	10	270	3	90.3	91.4	
18.6	15	130	10	280	1 1/2	23.0	23.2	
18.6	15	130	10	280	1	45.5	46.2	
18.6	15	130	10	280	2	89.6	93.0	
18.6	15	130	10	280	3	92.7	96.7	
18.6	15	130	10	290	1 1/2	32.8	32.8	
18.6	15	130	10	290	1	66.9	69.2	
18.6	15	130	10	290	2	90	95.0	
18.6	15	130	10	300	1 1/2	30.5	32.0	
18.6	15	130	10	300	1	87.7	92.7	
18.6	15	130	10	300	1 1/4	90.3	98.6	
10.9	8.7	100	8	300	1	88.7	91.8	
10.9	8.7	100	8	325	1	94.3	100.0	
10.9	8.7	100	8	340	1	94.0	99.0	
10.9	8.7	100	8	360	1	92.8	100.0	

An examination of the two curves (IV for iron, V for copper) in Figure 3, points to the effect of catalyst in speeding up the reaction. At higher temperatures, however, the effect of this catalyst is not so easily registered. It plays its greatest role at relatively lower temperatures. Thus, when experiments were conducted at the higher temperatures and for longer periods of time, our results were the same whether or



not a catalyst had been used, such reactions always running to completion if given sufficient time. In all these cases the degree of hydrolysis must be taken as indicative of the effect of catalyst; that is, the production of diphenyl oxide is just as much catalyzed as the production of phenol in the hydrolysis of benzene halides, and in most of the cases reported we had diphenyl oxide amounting to 6-10 per cent of the benzene halide used.

A number of different catalysts were now investigated in connection with these hydrolytic studies. Virtually none but metallic copper and cuprous oxide displayed anything like true catalytic properties. Cuprous compounds, when present, were considered as oxide in the presence of the caustic. Metallic copper seemed to possess a distinct ad-



vantage. It was little, if at all, affected by the reacting components at lower temperatures and its bright metallic surface functioned constantly in promoting the hydrolysis of these halides. The greater the surface exposed the more marked the catalysis. It is possible that alkali iodides and bromides did contribute slightly in a positive catalytic direction for this hydrolysis, but at the higher temperatures and for short operations their effect was negligible.

**EFFECT OF ADDED DIPHENYL OXIDE**—The well-known influence of esters and alkyl ethers in aiding the splitting off of halogens from organic compounds seemed to the senior author as possibly promising additional means of speeding up these hydrolytic reactions. In place of ordinary ether diphenyl oxide itself was now admixed with the reaction components before entering the bombs. Much to our surprise, the additional quantity of diphenyl oxide thus admitted did not show up as an additional quantity to the accustomed 6-10 per cent diphenyl oxide content in our final reaction product. This, of course, indicated a condition of equilibrium as existent in the system. Though this new interpretation was made in the first week of January, 1923, there had already been installed a small semiplant about 2 weeks before; hence a double opportunity of testing out the principle involved now lay before us.

From the work of Meyer and Bergius the hydrolytic effect of 3 mols of caustic soda in aqueous solution upon diphenyl oxide to give phenol was already known, but we had no idea that this rather difficult hydrolysis would proceed in low concentrations of caustic, and especially when even a great portion of this caustic already must have functioned to a large extent, during the initial heating step, in the neutralization of liberated acid and production of sodium chloride.

At this time the junior author undertook a study of the effect of diphenyl oxide additions in varying amounts to the reaction system as conducted at higher temperatures. These results are set forth in Table VI, and from them is plotted in Figure 4 the curve VI, based upon the diphenyl oxide introduced as against the yield in phenol, and also curve VII, based upon the diphenyl oxide introduced as against the total conversion of chlorobenzene. From experiment 9 it is clear that the addition of 2.6 grams of diphenyl oxide to 21.5 grams of chlorobenzene (a 12 per cent addition) resulted at 370° C. in a conversion of 95.7 per cent of the chlorobenzene and a yield of 96.2 per cent in phenol—values practically identical. This point at which the conversion



of halide is equal to the yield in phenol must be denoted by the intersections in the curves VI and VII. Thus we may conclude that the addition to a chlorobenzene-caustic alkali mixture of diphenyl oxide in an amount of approximately 12 per cent of the chlorobenzene present should result at 370° C. in complete conversion of the chlorobenzene and a yield in phenol calculated to 100 per cent when based upon the chlorobenzene.

Table VI—Hydrolysis of Chlorobenzene in Presence of Diphenyl Oxide in Rotating Iron Bombs (No Catalyst Used)

EXPT.	$C_6H_5Cl_2$ ( $C_6H_5$ ) <sub>2</sub> O		NaOH IN 8% AQ. SOLN.		TEMPERATURE ° C.	TIME Min.	CONVERSION %	YIELD PHENOL ON $C_6H_5Cl$ %
	Grams	Grams	$C_6H_5Cl$	Mols.				
1	21.5	4.0	18.6	2 1/4	370	32	92.1	99.4
2	21.5	3.0	14.0	2 1/4	370	33	93.6	99.8
3	21.5	2.0	9.3	2 1/4	370	34	94.8	92.0
4	21.5	1.0	4.65	2 1/4	370	33	96.0	88.0
5	21.5	0.0	0.0	2 1/4	370	33	95.1	83.5
6	21.5	2.0	9.3	2 1/4	370	36	98.4	98.6
7	21.5	4.0	18.6	2 1/4	370	38	99.3	108.7
8	21.5	2.0	9.3	2 1/4	370	35	96.8	94.8
9	21.5	2.6	12.0	2 1/4	370	35	95.7	96.2

In some cases, as in experiment 7, where a rather large proportion of diphenyl oxide was used, we note a further hydrolysis of this product and a yield in the phenol somewhat over 100 per cent, when based upon the chlorobenzene.

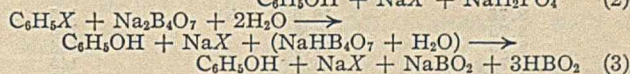
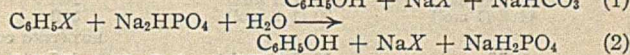
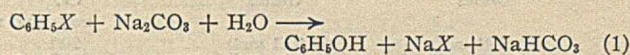
HYDRATION OF DIPHENYL OXIDE—Experiments were now undertaken to study the hydration of diphenyl oxide itself and a number of these are recorded in Table VII. Experiments 1 and 2 indicate the ineffectiveness of copper as a catalyst in the hydration of diphenyl oxide. Experiments 3 and 4, in comparison with experiment 5, indicate that the hydration may be equally as well accomplished by smaller amounts of alkali than are required to enter into combination with the phenol produced. The high percentage of phenol, when based upon the phenol actually required for combination with all of the caustic soda present, indicates, as in experiment 5, that the sodium phenate itself, in very dilute solutions, serves as an excellent hydrating agent. Its comparison with borax is given in Table VIII.

In the experiments given in Table VIII practically all of the phenol produced is found separated as free phenol upon the surface of the reaction product. It is here seen that the high alkalinity of sodium phenate carried the hydration of diphenyl oxide 46.4 per cent beyond the equivalent of phenol actually required for combination with one equivalent of caustic soda present. In experiment 2 the hydration of diphenyl oxide by borax produced only about one-half as much phenol as required for combination by the equivalent of one molecule of caustic soda theoretically possible. The manufacture of free phenol direct from its anhydride—i. e., diphenyl oxide—especially in crude state, becomes at once a possibility; steps covering such procedure have been made the subject of patent application by the authors.

EFFECT OF SALTS ON CHLOROBENZENE—The action of salts of strong bases and weak acids in effecting the hydration of diphenyl oxide prompted us to investigate further (in the spring of 1924) the effect of this same type of salts upon chlorobenzene. Tables IX and X present a series of such experiments.

The results prove conclusively the catalytic action of metallic copper in the hydrolysis of chlorobenzene by salts of strong bases and weak acids. Sodium carbonate functions here somewhat better than the other compounds. A temperature of 290–390° C. for one hour proved amply sufficient for complete hydrolysis. The salts of strong bases and weak acids, as here understood, comprise particularly that class of metallic salts which afford sufficient concentration of hydroxide ion in solution and which, after reaction with an organic halide, are usually converted into an acid salt or into some type of salt or salt mixture that cannot furnish sufficient hydroxide ion to promote further hydrolysis of the organic halide, nor of itself furnish anion to replace the acidic hydrogen of the organic hydroxide produced. True, a state of equilibrium is always present. In other words, the concentration of hydrogen ion of that portion of the free phenol in solution is balanced against the hydroxide ion of the aqueous salt mixture. Thus borax, in furnishing a certain quantity of hydroxide ion for the hydrolysis of chlorobenzene, is converted by the liberated hydrochloric acid into an acid borate, which immediately is changed into a staple metaborate and free metaboric acid. This mixture, now in equilibrium with tetraborate, no longer presents properties capable of furnishing sufficient hydroxide ion to aid the hydrolysis of chlorobenzene, nor sufficient sodium ion to produce sodium phenate. The phenol produced must therefore remain in the reaction mass as free phenol and can be separated therefrom by mechanical means. Traces of phenol that remain yet in solution of salt products are easily removed by a current of steam.

The action of sodium carbonate under the conditions just discussed leads directly to the production of sodium hydrogen carbonate, sodium chloride, and free phenol. Likewise trisodium orthophosphate and disodium orthophosphate react to give the monosodium phosphate, sodium chloride, and free phenol. Equations illustrating these reactions are given below (X represents halogen):



Practical application of the procedure just described will consist in the re-use of the neutral liquor left behind after

Table VII—Hydration of Diphenyl Oxide

EXPT.	BOMB	$(C_6H_5)_2O$ (1 mol)		NaOH		H <sub>2</sub> O Cc.	CONCN. AQ. SOLN. %	TEMPERATURE ° C.	TIME Hours	YIELD ON $(C_6H_5)_2O$ %	PHENOL BASED UPON REQUIREMENT FOR COMBINATION WITH NaOH %
		Grams	Mols	Grams	Mols						
1	Rotating iron (no catalyst)	33	17	17	2 1/4	183	8	370	2	80.5	74
2	Rotating copper	15.7	8.3	8.3	2 1/4	88	8	370	2	79.2	72
3	Rotating copper	33	17	17	2 1/4	183	8	360	1	44.5	41.5
4	Rotating iron (no catalyst)	19.6	10.4	10.4	2 1/2	120	8	325	1	10	8.3
5	Rotating iron (no catalyst)	42	5.3	5.3	1/2	225	2.3	345	1/4	33.8	125

Table VIII—Hydration of Diphenyl Oxide in Rotating Iron Bombs, without Catalyst

EXPT.	SALT USED		$(C_6H_5)_2O$		H <sub>2</sub> O Cc.	CONCN. AQ. SOLN. %	TEMPERATURE ° C.	TIME Min.	YIELD PHENOL ON $(C_6H_5)_2O$ %	PHENOL BASED ON REQUIREMENT FOR COMBINATION WITH NaOH <sup>a</sup> %
	Grams	Mol	Grams	Mols						
1	$C_6H_5ONa$	21.5	1.5	21 (1 mol)	230	8.6	370	35	35.3	146.4
2	$Na_2B_4O_7 \cdot 10H_2O$	71.5	1.4	21.5 (1 mol)	225	15	370	40	39.5	53 (on 1 equiv. NaOH)
3	$Na_2CO_3$	45	2.2	33	255	15	372	40	10.0	9 (on 1 equiv. NaOH)
4	$Na_2CO_3$	30	1.6	30	270	10	370	90	12.1	15 (on 1 equiv. NaOH)

<sup>a</sup> Present as phenate.

removal of free phenol. To this liquor caustic soda in correct molecular proportions is now added, and the original salts are thus brought again into consideration, though in this instance with certain amounts of alkali halide held in solution. After a number of operations are conducted, it becomes necessary to remove the excess of alkali halide by the ordinary evaporation methods.

In Figure 3, curve VIII, there is shown the hydrolysis of chlorobenzene by an aqueous solution of sodium carbonate, over a short range of temperature in the neighborhood of 300° C. and in the presence of copper. It is here seen that the hydrolysis of chlorobenzene proceeds equally as well, if not a little better, with sodium carbonate (1 $\frac{1}{4}$  mols) than with caustic soda, even with 2 $\frac{1}{4}$  molecular equivalents; the latter case necessitates, as already known, a complete acidification of the reaction product, whereas with sodium carbonate there is no need of acidification.

**BASIS OF PATENT APPLICATIONS**—This discovery of a new method for manufacture of free phenol is embodied in patent applications by the senior author with J. W. Britton, and in further patent application by the senior author with E. C. Britton, in which latter application the addition of diphenyl oxide to the sodium carbonate-chlorobenzene reaction mixture is shown to lead to a constant yield of 100 per cent phenol, with complete hydrolysis of chlorobenzene. In general, we now have the evidence that there is existent in

high yields in phenol obtained by the early investigators under a prolonged heating of benzene halide-caustic soda mixtures. At no time can we consider the hydration of diphenyl oxide into phenol through the catalytic action of hydroxide ion as approaching completion, except possibly in the presence of an undepleted high concentration of this hydroxide ion. In the light of this study many of the apparent inconsistencies in the literature become easily explicable.

In a closely analogous situation Schwalbe<sup>32</sup> encountered this effect of salts of strong bases and weak acids in his studies of  $\beta$ -thionaphthol production by action of a 50 per cent aqueous solution of potassium sulfhydrate in excess upon sodium  $\beta$ -naphthalene sulfonate when heated to 200–220° C. under pressure. An appreciable amount of  $\beta$ -naphtholate was here produced, especially at the higher temperature; a still larger amount was produced when the alkali solution contained 50 per cent potassium sulfide. The well-known ease of hydrolysis of potassium sulfide accounts for his results, a condition likewise favored even with potassium sulfhydrate alone at the higher temperature in that its transformation into potassium sulfide and hydrogen sulfide is aided. Whatever  $\beta$ -naphthol and  $\beta$ -thionaphthol came into existence must immediately have reacted with the alkali sulfhydrate to liberate hydrogen sulfide and enter into combination with the alkali itself, since the preliminary

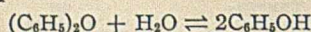
Table IX—Effect of Salts on Hydration of Chlorobenzene

EXPT.	CATALYST	C <sub>6</sub> H <sub>5</sub> Cl Grams	Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> ·10H <sub>2</sub> O		NaOH (1 mol)	H <sub>2</sub> O Cc.	CONCN. Aq. SOLN. %	TEMPERATURE ° C.	TIME Min.	PHENOL (FREE) %	CONVERSION %
			Grams	Mols							
ROTATING IRON BOMB											
1	None	21.5	73	1	8	250	2.4% NaOH, 11.7% Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub>	370	35	70.4	89
2	None CuCl	16.1	60	1.2	0	250	11.5	370	40	56	69
3	0.5 gram	12.3	41.7	1.2	0	230	8	370	60	84.2	94.4
4	None	12.3	41.7	1.2	0	230	8	370	60	52.7	65.3
5	None	21.5	Na <sub>2</sub> HPO <sub>4</sub> ·10H <sub>2</sub> O 63 0.9		0	200	11.6	360	60	4.8	5.6
ROTATING COPPER BOMB											
6	Cu	4.9	31.2	2	0	92	10	280	60	17.3	17.5
7	Cu	4.9	31	1	9	215	13.4	370	60	34.8	42
8	Cu	7.6	18.3	2	2.7	97	2.45% NaOH, 10% sodium acetate	280	60	40.5	42

Table X—Effect of Sodium Carbonate on Hydration of Chlorobenzene

EXPT.	C <sub>6</sub> H <sub>5</sub> Cl Grams	Na <sub>2</sub> CO <sub>3</sub> Grams	H <sub>2</sub> O Cc.	CONCN. Aq. SOLN. %	TEMPERATURE ° C.	TIME Min.	PHENOL (FREE) %	CONVERSION %
ROTATING IRON BOMB								
1	21.5 (1 mol)	20.3 (1 mol)	200	9.2	370	60	23.8	37.9
2	44.8 (1 mol)	50 (1.2 mol)	300	14	370	72	60.7	87
ROTATING COPPER BOMB								
3	8.75	16.5 (2 mols)	146	10	340	60	89.4	100
4	8.75	16.5	146	10	340	60	88.0	99
5	8.75	16.5	146	10	320	60	91.2	100
6	8.75	16.5	146	10	300	60	88.8	95
7	8.75	16.5	146	10	300	60	87.9	94
8	8.75	16.5	146	10	290	60	83.7	86.5
9	8.75	16.5	146	10	280	60	67.9	69.4
10	13.2	15.5 (1 $\frac{1}{4}$ mols)	150	9.4	300	60	85.8	95
11	13.2	15.5 (1 $\frac{1}{4}$ mols)	150	9.4	300	60	83.7	94.4
12	13.2	15.5 (1 $\frac{1}{4}$ mols)	150	9.4	320	60	84.9	100

our reaction system a condition of equilibrium, as represented by the equation



At the higher temperatures and under influence of metallic oxides phenol tends to lose water and pass into diphenyl oxide. When in aqueous solutions the concentration of hydroxide ion is reduced to a minimum, we also note the backward trend in the equilibrium above (in confirmation of the observations of Meyer and Bergius); on the other hand, in the presence of increasing concentration of hydroxide ion diphenyl oxide tends to pass into phenol by hydration. The action of sodium phenate as an end product is almost as effective at higher temperatures in providing hydroxide ion as is sodium hydroxide, and hence always those comparatively

step of acidification was always required by Schwalbe for the liberation of his end products.

Meyer and Bergius<sup>22</sup> noted the production of small amounts of phenol by the actions of such salts as sodium carbonate in aqueous solution upon chlorobenzene at 300° C., but these hydrolyses were conducted under such conditions that any appreciable quantity of free phenol failed to attract notice. Had these investigators examined their aqueous reaction products as to the presence therein of sodium hydrogen carbonate and its inability to suffer metathesis with free phenol, thus making possible the direct conversion of chlorobenzene into phenol, they might have turned their researches in this direction. Practical application of this type of hydroly-

<sup>32</sup> *Ber.*, 39, 3102 (1926).

sis is dependent upon complete conversion of benzene halides and the employment of such anions as will not suffer replacement in aqueous media by phenoxyl ions. Alkali-sulphydrates at once fall out of consideration for use in preparation of phenol, not alone by reason of the instability of alkali sulphydrates in presence of free phenol, but also because of their distinct tendency to function primarily in thiophenol production. Had Schwalbe, on the other hand, employed a high concentration of hydrogen sulfide in the bomb containing the alkali sulphydrate-naphthalene derivative mixture and operated at a slightly higher temperature, he would have obtained a complete conversion of his  $\beta$ -naphthalene sulfonate and a quantitative yield of free  $\beta$ -thionaphthol; under such conditions it may be inferred that the sulphydrate ion would not suffer appreciable replacement by thionaphthoxyl ion to give alkali thionaphtholate.

A patent was granted to the authors<sup>33</sup> for a method of manufacturing phenolic compounds under the procedure indicated in Table VI. The principle herein set forth directs that diphenyl oxide must be added to the reaction mixture of benzene halide and dilute caustic soda solution in just that quantity which of itself will be found to have formed when this reaction mixture is heated alone. This quantity ordinarily approaches 10 per cent of the benzene halide employed and, when present in the reaction mixture, operates as a repressant to the further formation of diphenyl oxide. In other words, a state of equilibrium is here established and no more diphenyl oxide will be produced than is definitely fixed by the conditions of the reaction. Our early attempts to speed up the hydrolysis of benzene halides by the addition of this ether found little hope of verification in the present situation. Possibly at lower temperatures, where little or no hydration of diphenyl oxide is apparent, we may have had a slight positive catalytic effect due to its presence.

#### Investigations on Semiplant Scale

During 1923 the semiplant for study of phenol manufacture from benzene halides experienced one continual make-and-break-down operation. This little plant was constructed upon the continuous system, with heavy iron tubes ( $3/8$  inch i. d. and  $3/4$  inch o. d.) which were heated at first by means of a sodium nitrite bath. Several stoppages within the tubes, necessitating Herculean efforts to remedy the same when all was encased in sodium nitrite bath, spelled the doom of any such means of heat supply. A hot-air furnace was next installed. This procedure is applicable when great care is taken in baffling the heat inlet.

The pumps employed in this semiplant were of special design in the high-pressure field. They were connected directly to the tubular system and operated under a pressure from 3000 to 4000 pounds per square inch.

The rotation of the bombs in the research laboratory afforded abundant opportunity for a study of mixing conditions necessary to secure the best reactions. These bombs could be rotated at 60 r. p. m. (when a point on the inner surface of bomb traveled 23 feet per minute) and on down to 22 r. p. m. (when a point on the inner surface of bomb traveled 8.5 feet per minute). When 1 mol of bromobenzene and  $2\frac{1}{2}$  mols of caustic soda solution of 8 per cent concentration were heated to  $250^\circ\text{C}$ . under the more rapid agitation, complete conversion resulted in 1 hour; when this experiment was repeated at the lower rate of agitation stated above, complete conversion likewise resulted in 1 hour. When the same experiment was repeated without agitation complete conversion required  $2\frac{1}{2}$  hours. It was concluded, therefore, that only a very moderate degree of agitation suffices for complete reaction of the components.

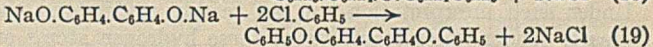
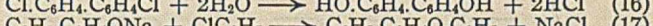
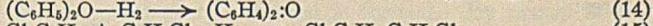
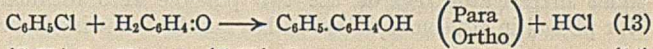
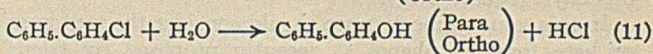
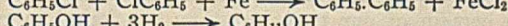
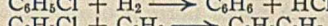
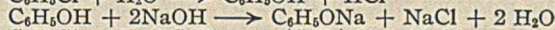
When this problem of agitation was transferred to the plant, in which a continuous system was presented, we were confronted with the question of turbulence as set up in the tubes under definite velocity of flow or reacting components. The desired degree of turbulence could not be reached until larger tubes were installed. By this stepping up into larger tubes our semiplant became at once a unit in the manufacturing plant of today.

#### Chemical Considerations

The study of the reaction products as obtained in the hydrolysis of benzene halides by caustic alkali, under plant conditions, has presented a mass of interesting data, much of which is yet to be unraveled. We shall now consider the possible chemical reactions and attempt to account for all the products which may result from secondary interactions.

The experimental work in bombs did not reveal the extent to which secondary reactions were able to proceed. However, when the analysis of plant waste disclosed the presence of certain organic compounds, it was usually possible to secure from a repetition of bomb experiments (in duplicate or triplicate) a weighable quantity of tarry material sufficient to confirm the analysis of the plant waste. Certain discrepancies in these analytical figures must be attributed to the difference in methods of operation in the plant and in the research laboratory.

The complete set of equations which we have had to consider is now given below:



Equations (1), (2), and (3) depict the main trend of reaction when a benzene halide is hydrolyzed by caustic soda. When there is insufficiency of caustic it has already been shown that equation (3) is decidedly pronounced. The actual concentration, however, of the diphenyl oxide in reaction product will be determined by governing factors already discussed as applying to the equilibrium expressed in equation (4).

Equation (5) introduces the element hydrogen, a most unwelcome factor but one that must be brought under control if we would operate this type of phenol synthesis. As only metals can be expected to withstand the high pressure called into play, it becomes our duty to select the best conditions under which to operate without the possible production of excessive hydrogen in nascent form. Iron is naturally preferable. The incrustation of magnetic iron oxide on the interior walls of tubes will protect these tubes, but much fluctuation in the heat applied to these tubes will initiate a peeling off of portions of this incrustation and hence bring

<sup>33</sup> U. S. Patent 1,607,618 (November 23, 1926).

new surfaces of iron in contact with caustic liquor for further production of nascent hydrogen.

In the small semiplant, owing primarily to improper mixing of reacting ingredients, there was such a pronounced evolution of hydrogen that this gas could be kept in a continuous large flame at the exit of the tubular system. The more concentrated the caustic the more pronounced is this production of hydrogen. With any concentration of caustic soda over 11–12 per cent, it is well-nigh impossible to operate in iron tubes and expect these tubes to continue long in service.

The action of nascent hydrogen on chlorobenzene in the presence of metals is known to give good results in the reduction of this halide to benzene. The presence, however, of chlorobenzene along with the benzene produced from it by reduction makes further for a coupling up of these two distinct molecules in the presence of alkali and eliminating therefrom hydrochloric acid, with final production of diphenyl (equation 7). Furthermore, diphenyl is supposed to be brought into formation whenever chlorobenzene alone is brought in contact with an overly-heated portion of metal (equation 8).

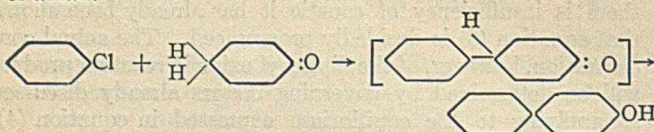
The most undesirable effect of nascent hydrogen in contact with certain metals and free phenol (there is always free phenol in sodium phenate liquors) is the reduction of phenol to cyclohexanol (equation 9). This product undergoes further decomposition (pyrogenic) and is registered usually as tar, at the tar end of the distillation steps. When we consider pyrogenic decomposition, we can account for the naphthalene and similar compounds whose presence in these hydrolytic reactions was confirmed by Meyer and Bergius.

When hot chlorobenzene is brought suddenly into contact with caustic soda, we encounter the same type of coupling as shown in equation (7), but with the production of *p*-chlorodiphenyl (equation 10). A small portion of *o*-chlorodiphenyl is likewise produced. These products have been identified in certain of our tars, but they are found more often as hydrolyzed into the corresponding *p*- and *o*-hydroxydiphenyls (equation 11).

In this same connection we should consider the tautomeric or keto form of phenol as recently proposed by Glenz<sup>34</sup>. This investigator regards the two possible keto formulas for phenol in aqueous solution as having the following structures:



Under such interpretation we can readily understand the greater tendency for reactivity of these hydrogen atoms on the reduced nuclear carbon atom, and hence condensation with chlorobenzene might easily proceed under the influence of alkali.



Hydroxydiphenyl constitutes one of the main ingredients of the waste tar left after the phenol and diphenyl oxide have been removed from the reaction mass. It is estimated that from 20 to 25 per cent of the tar waste is made up of mono-hydroxydiphenyl compounds, of which at least three-fourths consists of *p*-hydroxydiphenyl. Whichever of the two explanations above is accepted as leading to its production, it is well established that copper possesses a particular aptitude to speed up its formation. The actual isolation

of chlorodiphenyl may be taken as pointing to this source of its production; yet at higher temperatures we are inclined to favor the second interpretation, especially by reason of its production where the relative concentration of chlorobenzene is low and that of sodium phenate is very high.

The preparation of *p*- and *o*-hydroxydiphenyl on a large scale by the use of extensive surfaces of metallic copper in a reaction mixture of benzene halides and caustic alkali, or alkaline-earth hydroxides, in aqueous solution, is a simple matter from the manufacturing standpoint. The installation of equipment for its manufacture on an extensive scale awaits only the creation of an industrial demand.

The presence of overly-heated metallic oxides in contact with the benzene halide-caustic soda mixture contributes further to the formation of several by-products. As shown in equation (15), chlorobenzene can be condensed with itself by elimination of two hydrogen atoms from the position para, and possibly ortho, to the chlorine, and thus a *p*, *p'*-dichlorodiphenyl, as well as an *o*, *o'*-dichlorodiphenyl, comes into place. These compounds in turn suffer halogen hydrolysis and become *p*, *p'*-dihydroxydiphenyl and *o*, *o'*-dihydroxydiphenyl, respectively (equation 16). The dihydroxydiphenyls are easily identifiable in the tars and possibly amount to as much as 2–3 per cent of the total waste, but of this fraction the greater portion is *p*, *p'*-dihydroxydiphenyl. The presence of more active metallic oxides will, of course, be expected to increase considerably the formation of isomeric polyhydroxydiphenyl derivatives.

In the same manner diphenyl oxide (14), by the action of metallic oxides, may be made to suffer the loss of two hydrogen atoms from its two phenyl groups and give rise to diphenyl oxide (14); only minute quantities of this substance have been isolated from our tar wastes.

In equations (17), (18), and (19) are shown only three of the distinct condensations illustrative of tertiary by-products. Such end products do occur in the higher boiling fractions of the waste tar.

In summing up these considerations, we should emphasize that waste tar in the hydrolysis of chlorobenzene is not appreciably high but may become so unless proper operating conditions are carefully followed. Our bomb experiments indicated only minute portions of tarry material, but in the plant appreciably more tar has been produced. Though at present we find no more tar than we usually obtained in the well-known sulfonation process, we confidently expect such advanced methods of heat supply that will eliminate all undesirable products.

#### Criticism of Early Researches

After several years of investigational work both in laboratory and semiplant, we find ourselves in better position to diagnose the difficulties encountered by preceding investigators.

At the outset mention should be made of the unreliability of analytical procedure as affecting the determination of phenol present in mixtures of the sort here concerned. Titration with potassium bromate-potassium bromide solution fails to take account of the hydroxydiphenyl and other phenolic compounds which accompany phenol of high-temperature and high-pressure hydrolytic origin. Even the diphenyl oxide also present will respond to this method of titration unless particular care is exercised to eliminate undesirable conditions. The most reliable determinations are obtained when titrations are conducted in presence of a 5 per cent excess of potassium bromate-bromide solution at the lower temperature of 20° C. and not more than 1/2 to 1 minute reaction time is allowed to elapse before titrating back with sodium thiosulfate solution. The analyses, there-

<sup>34</sup> *Hels. Chim. Acta*, 6, 832 (1923).

fore, as recorded in the literature cannot always be taken as conclusive.

The use of metallic copper as catalyst for the splitting off of halogen from aromatic halides was originally proclaimed by Ullmann, and all researches since then have substantiated his findings. Torley and Matter emphasize the advantage of extensive copper surfaces. Meyer and Bergius ably proved the need of rotating bombs to insure increased hydrolysis, and following their reports no investigators of repute have essayed to publish hydrolytic results without thorough mixing of reacting components. Though the work of Meyer and Bergius indicated possibilities of practical application for synthesis of phenol from chlorobenzene, all hopes in that direction were shattered when an outlet for diphenyl oxide failed to materialize.

The use of methanol as an aid to these hydrolytic reactions through general solvent action, as disclosed in several of the first patents, could not have met with commercial success, by reason of the great quantity of methyl ether which we have observed is always simultaneously produced by dehydration of this alcohol in the presence of metallic oxides and caustic under pressure. When an outlet for methyl ether presents itself this type of hydrolysis may enter into further consideration.

The introduction by Aylsworth of the continuous system for hydrolytic studies appeared, indeed, most promising. Our semiplant was first constructed along lines in keeping with these recommendations. The difficulties that beset us must certainly have beset all others so minded to experiment in a large way.

Employment by Aylsworth of fairly strong caustic in hot steel tubes has already been noted as leading directly to blow-outs through the increased action of such caustic (over 18 per cent concentration) upon iron surfaces intermittently exposed. Furthermore, the excessive hydrogen here resulting from the interaction of iron and the aqueous liquor contributes to a greater production of reduced compounds, all of which easily suffer pyrogenic decomposition into tarry material. This tendency to tar formation is augmented, not only by the fairly concentrated caustic, but particularly by his method of recirculating a portion of the hot resultant liquors after mixing with incoming reaction ingredients. Such procedure alone would have spelled the doom of the process. By operating in this manner a high concentration of hot sodium phenate and diphenyl oxide was brought in contact with chlorobenzene and caustic as yet unheated, the diphenyl oxide aiding the intersolution of phenate and chlorobenzene. Chemical reactions under such conditions are found to promote rapidly the formation of diphenyl oxide and hydroxydiphenyl, and thus the only hope of successful operation is a reliance upon stronger caustic at higher temperatures as a means of hydrolyzing this excessive diphenyl oxide.

Our results confirm the need of employing these higher temperatures for this end, but they further indicate that the lower the temperature can be held (preferably 340-350° C.) the more nearly does the percentage of total phenol approach that of total conversion—a status indicative of perfect efficiency.

The Aylsworth system, if ever put into practice, would lead to such an amount of diphenyl oxide and tar that it is safe to estimate that no more than a 70 per cent efficiency on phenol over all could possibly be maintained.

In view of the foregoing statements, and most decidedly in emphasis of the complicated secondary and tertiary reactions set up in a continuous system of the type under discussion, the conclusion is inevitable. The processes devised up to 1924 for the manufacture of phenol through high-

temperature hydrolysis of benzene halides, either by means of a continuous system or in autoclave, offered no commercial possibilities. The Aylsworth contribution of hydraulic accumulator for maintaining the liquor at constant pressure might have saved the day for the continuous system had there been some practical means of attaining a reasonable degree of efficiency. The use of sodium nitrite as a heating bath in large-scale practice cannot command serious attention. The hydraulic accumulator, however, actually performs as stipulated but it is too cumbersome to withstand long the inroads of invention.

### Conclusions

The development at the Dow Chemical plant making for introduction and use of a diphenyl oxide boiler is heartily endorsed by Herbert H. Dow,<sup>35</sup> as an ideal method of transmitting heat to a system metallically enclosed, the rate of heat transfer from condensing vapor to heating surface being far in excess of that from hot liquid thereto. It is to this invention that the phenol plant is now looking for means of securing an evenly distributable and controllable heat supply. When such device is finally perfected, there will open up before us a new era in the study and application of organic chemical reactions.

With so many difficulties confronting us in the application of high-temperature hydrolytic studies, let it not be surmised that no ray of hope appeared on the horizon. This hope lay in the use of diphenyl oxide admitted into the reaction mixture. Diphenyl oxide and benzene halides are mutually miscible and together emulsify with aqueous caustic. Diphenyl oxide restrains the benzene halide from going too far astray. The nefarious influences, so prone to assert themselves, are parried, as it were, by the heavier and more refractory molecules. The action of diphenyl oxide in repressing more of its kind from entering the system has already been discussed. It further serves to render inert the rough metallic oxide incrustation by interposing its protective oily coating between this oxide and the reactants.

What has been said for the benzene halides, both in bomb and circulatory system, is also true for benzenesulfonic acid in its interaction with caustic soda. The hydrolysis proceeds here equally as well in aqueous solutions under pressure as it does in molten state at normal pressure. An abundance of tarry material is formed. By reason of the homogeneous nature of the solution it might be expected to proceed somewhat more rapidly and smoothly than the corresponding benzene halide-caustic soda mixture; the opposite, however, has proved to be the case. The reaction runs with greater difficulty and requires longer time for completion, as evidenced likewise by the work of Willson and Meyer,<sup>36</sup> who obtained a 60 per cent yield in phenol by interaction of caustic soda upon sodium benzenesulfonate in aqueous solution when heated at 320° C. for 72 hours under pressure. Diphenyl oxide is produced in the system in the same way and in approximately the same amounts as already recorded with benzene halides. The process, therefore, is equally impractical from a commercial standpoint. However, the addition of diphenyl oxide to this benzenesulfonic acid-caustic soda system has been found to function in exactly the same way and to the same end as already described for high efficiency in the benzene halide-caustic soda system; a patent application by the authors, covering these points, is now pending.

The comparatively recent research by Rosenmund and Harms,<sup>31</sup> relating to the hydrolysis of benzene halides by salts of strong bases and weak acids in aqueous solution,

<sup>35</sup> *Mech. Eng.*, **48**, 815 (1926).

<sup>36</sup> *Ber.*, **47**, 3160 (1914).

is found, upon inspection, to have missed the principle of free phenol liberation *in cursu*. This, no doubt, came about through the use of additional reactants, such as calcium carbonate and the like; at least, the preliminary step of acidification is described as necessary to set free the phenol. In our experiments connected with the use of salts of strong bases and weak acids, we make no addition of acid to reaction product for the purpose of liberating phenol; the phenol is already there in the free state. This new type of phenol manufacture, with copper as a catalyst, requires not so high a temperature as by use of caustic soda on the same halides. The introduction, therefore, of the benzene halide-sodium carbonate mixture into a continuous system offers a great improvement over the former processes. Above all is this to be approved by reason of the fact that sodium carbonate solution contributes in far less degree than caustic soda to the production of hydrogen in closed metallic systems.

Organic chemical reactions under high pressure are now in the first stage of development. The difficulties that have attended the employment of hot caustic liquors within metal tubes have demanded our constant attention. Already a marked improvement in the continuous system, as heretofore described, is before us. The invention, as such, is made the subject of patent application by the senior author now pending. It consists primarily in the employment of a set of tubes for intake of the caustic on the one hand, and a set for the intake of organic compounds on the other. Each tubular system will be constructed of properly selected material. Thus, the caustic soda solution will preferably be supplied through heated copper tubes; the benzene derivatives will be supplied cold and through any sort of tubing. The two reactants will be pumped into copper or copper-lined autoclaves, either in individual or continuous set-up, and the heat supply in the caustic will be made to suffice for the completion of the hydrolysis of organic derivatives. Following this stage, either by cooling directly or pumping through an additional continuous system, discharge will

be made and the final liquor worked up for hydroxy aromatic compounds.

In the procedure just outlined it will be noted that little if any overheating of organic derivatives is possible. Rapid and complete hydrolysis will be highly favored from the start. The time of actual reaction will be reduced to a minimum, possibly from 3 to 5 minutes for a benzene halide-caustic soda mixture.

In the midst of experimental work with constant attention upon results carried out over monthly periods, it is yet too soon to state that our process is just so and so. That is exactly what it is not. As to the relative merits of the new process as compared with the old sulfonation process, this is a matter of individual opinion. Whatever the disparagement in prices between chlorine and sulfuric acid as intermediary reactants, this is of no concern to chlorine manufacturers; and as for labor, the sulfonation process really requires an abundance—the new process runs almost by itself.

#### Acknowledgment

Many of the experimental data presented in this paper have been taken from the reports made to The Dow Chemical Company by William H. Williams and Joseph W. Britton. The authors hereby acknowledge their indebtedness to these industrious members of our Organic Research Division. We wish further to express to Thomas Griswold and the Engineering Department, and to Mark E. Putman of the Production Department, our highest appreciation for the keen interest and assistance they have always rendered in the unraveling of complexities that were wont to confront us. And, to the long line of investigators who have striven to establish the practicability of benzene halide hydrolysis, we would express our admiration of their each and every effort. Finally, it can be written that their efforts and ours have produced a new successfully operating synthetic phenol plant that will afford the arts and industries a chemically pure phenol at lowest prices.

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## Measurement of Surface Temperature<sup>1</sup>

D. F. Othmer and H. B. Coats

DEPARTMENT OF CHEMICAL ENGINEERING, UNIVERSITY OF MICHIGAN, ANN ARBOR, MICH.

THE study of the rate of heat transfer is no longer merely one of over-all coefficients—from the heating to the cooling medium—but has become instead the study of individual film coefficients. The concept of at least a single stagnant film on each side of a metal wall dividing the two fluids at different temperatures is generally accepted. These films may be considered to transfer heat entirely by conduction and, because of the low thermal conductivity of the fluids, divide between them almost the entire difference between the temperatures in the bodies of the two fluids. The high thermal conductivity of the metals used in tubes as compared with that of any fluid film makes the temperature drop across the tube almost negligible for work with any degree of accuracy yet attained. For example, in the case of steam condensing on one side of a tube to heat a liquid on the other, the tube may usually be considered radially isothermal. An accurate measurement of this tube temperature is essential for calculating the film coefficients. Since the temperatures of the two fluids and the amount of

heat passed through the tube wall can usually be obtained very simply, the only difficult measurement is that of the tube temperature. Lack of general agreement between investigators with regard to film coefficients is probably due to faulty tube-temperature measurement.

#### Previous Work

An accurate means of measuring tube temperatures was desired by one of the authors as a first requisite in the study of the rate of condensation of steam. A number of methods have been published, which will be briefly reviewed for comparison. This is not a complete bibliography; in fact, some of the methods found were so obviously crude or inaccurate as to deserve no consideration. A case in point is the use of plugs of easily fusible alloys sunk in the metal. The metal temperature was taken at the end of an experiment as the mean between the known fusion temperature of the last plug to fuse and that of the one with the next higher melting point which did not fuse.<sup>2</sup>

MERCURY THERMOMETERS—The use of mercury thermom-

<sup>1</sup> Received December 15, 1926; revised paper received November 5, 1927.

<sup>2</sup> Durston, *Trans. Inst. Naval Arch.*, 1893, 130.

eters to measure temperature comes first to mind, but their only successful use in measuring tube temperatures was by Callendar and Nicolson,<sup>3</sup> who condensed steam in a cast-iron cylinder, 1 inch inside diameter and 5 inches outside diameter, drilled for thermometer wells parallel to the axis. Cooling water was circulated around the outside, and the temperatures at various distances from the condensing surface were read from thermometers in these wells. By plotting radial distance against temperature, the temperature of the condensing surface could be read by extrapolation.

**ELECTRICAL RESISTANCE**—In the same journal Callendar reported the measurement of the temperature of a platinum tube 0.25 by 16 by 0.006 inches by changes in its electrical resistance. In this case he passed water through the tube and condensed steam on the outside. The refinements required to measure the very small electrical resistance of a tube approaching commercial dimensions have so far prevented a further application of this method, but a careful experimenter would probably find it capable of producing very good results.

**EXTENSOMETER**—The expansion of a body with change of temperature is the property usually used to measure or regulate temperature. The direct measurement of the linear expansion of a tube as a means of estimating its temperature was used by Stanton.<sup>4</sup> His extensometer could be read to 0.1° F., but he found it necessary to calibrate it before and after every experiment because of uncertainty of the metallic expansion. The extensometer method was also used by Soenneken<sup>5</sup> with a more elaborate apparatus, which he also found was accurate only if frequently recalibrated. This method, like the two previous ones, is obviously to be used only with experimental apparatus especially designed with reference to the method of temperature measurement, and as such has only a very limited application.

Sucksmith<sup>6</sup> indicates a large refinement on any previous work with an extensometer, although he did not measure tube temperatures. He applied the ultramicroscope to the measurement of small increments of temperature.

**THERMOCOUPLES**—Thermocouples have been the most common means of measuring tube temperature because of their applicability to distant reading. It is always possible to devise a method of running wires to the junctions, but this entails a complication which must be overcome before the use of thermocouples can even be considered. The leads to the junction on the tube, after leaving the tube surface, must traverse a zone of higher or lower temperature than that of the tube itself. This results in a conduction of heat along the wires, which in turn causes an increase or decrease in temperature at the junction of the wire with the tube wall. That this causes a very serious error has been shown by several previous experimenters and by some trials in this laboratory, in which the thermocouples formed by simply sealing the two wires in the tube wall indicated a temperature closer to that of the steam than the known temperature of the tube found by another method.

Several experimenters have minimized this difficulty by shielding the small section of tube where the thermojunction

is installed. Jordan<sup>7</sup> and Webster<sup>8</sup> have attached a small tube tightly against the surface of the main tube and brought their thermocouple wires out through this. The former pressed his junctions against the surface of the tube, and the latter pressed them into small holes in the tube. This method may be of value where it is applicable, but the disturbance of the surface is so great as to threaten the accuracy of the reading when a very large amount of heat is passing through the tube wall.

King and Blackie<sup>9</sup> used a thermocouple, with a radiation screen behind it, pressed against the wall of a boiler or other hot surface. They considered it reliable only within  $\pm 5^\circ$  C. up to 160° C. It was not intended to be used on tubes. An improvement on this method is that of Boyer and Buss.<sup>10</sup> The application of this thermocouple to the measurement of tube temperatures is not mentioned, but a modified form might be devised which would, however, probably indicate, not the average temperature of the tube, but a slightly higher one.

For determining the thermal conductivity of iron, Hall<sup>11</sup> copper-plated the top and bottom of a cylinder of the metal to a thickness of about 2mm. Copper wires were attached to the top and bottom surfaces, which were maintained at different temperatures with hot and cold water. The thirteen different thermocouples so formed varied among them-

selves by an amount equal to 8 to 10 per cent of the total temperature drop from top to bottom of the iron.

The methods of attaching thermojunctions experimented with in this laboratory include (1) soldering wires to surface of tube; (2) soldering wires together and then to walls of a small hole in the tube; (3) soldering wires in separate holes in tube; (4) swaging wires in small holes; (5) butt-welding wires and soldering the junction in a slot in the tube; (6) soldering or welding wires to a butt junction, insulating all but this junction with fine asbestos fiber and soldering this junction in a hacksaw slot in the tube wall.<sup>12</sup> The insulation of method (6) was covered with solder and the whole surface (as also the previous ones) was filed smooth. The tubes on which these wires were fastened were mounted so that steam condensed on the outside and cooling water circulated on the inside with the wires drawn out of the steam space through a packing gland. Concordant results could not be obtained even among several couples put on in the same manner, and all methods but (6)<sup>12</sup> gave a temperature drop much higher than was expected. The error in the readings was due to localized heating of the tube by heat conducted along the thermocouple wire from the steam. Discrepancies between several couples put on by method (6) were not so large, but amounted to differences of from 5 to 15 per cent of the total temperature drop from steam to tube.

#### Electrodeposition Method

The method finally adopted depended on the embedding of wires in an electrodeposited layer of the same metal on the surface of a tube of a second metal. In effect this provided a comparatively broad interface—i. e., a part of the

Methods for attaching thermocouples to heating surfaces by mechanical means may give satisfactory results, but may also give very erratic results. If the junction is formed by plating a layer of the second metal on the surface whose temperature is to be studied, and if the leads are attached before plating so that they are imbedded in the plate, uniform results are obtained. Directions are given for making nickel-copper junctions on tubes.

<sup>1</sup> *Engineering*, 64, 481 (1897).

<sup>2</sup> *Trans. Roy. Soc. (London)*, A190, 67 (1897).

<sup>3</sup> *Mitt. Forschungsarbeiten*, 108-109, 33-78 (1911).

<sup>4</sup> *Phil. Mag.*, [6] 43, 223 (1922); see Whiddington, *Ibid.*, [6] 40, 634

(1920).

<sup>7</sup> *Proc. Inst. Mech. Eng. (London)*, 1909, 1317.

<sup>8</sup> *Trans. Inst. Eng. Shipbuilders Scotland*, 1713, 57.

<sup>9</sup> *J. Sci. Instruments*, 2, 260 (1925).

<sup>10</sup> *Ind. Eng. Chem.*, 18, 728 (1926).

<sup>11</sup> *Am. Acad. Arts Sci.*, 34, 283 (1898).

<sup>12</sup> Devised and utilized by L. A. Phillips in this laboratory.

surface of the tube—for one junction of the thermocouple. A second wire of the same metal as the tube was either similarly embedded in an electrodeposited plate of its metal on another section of the tube or pressed against an unplated spot on the tube. The cold junction was made in the usual manner, and the wires were connected to selective switches and thence to a potentiometer.

#### Metals Used

Since only pure elementary metals can be used in this type of thermocouple, the first to suggest themselves are copper and nickel. For example, a copper tube may have nickel wires embedded in a nickel deposit plated on its surface for one side of the circuit and a copper wire pressed or copper-plated to an unnickelled spot for the other side. The nickel wires are then welded or soldered to copper wires leading to the potentiometer and these junctions kept in an appropriate ice bath.

A metal which would remain unoxidized and constant in regard to surface conditions affecting the rate of heat transfer was necessary and nickel fulfills that requirement better than copper.

*Note*—Badger, "Heat Transfer and Evaporation," p. 134; Chemical Catalog Company, 1926, shows that copper is liable to oxidation, which renders consistent experimental results unobtainable. Later work in his laboratory, as yet unpublished, shows that after a time the surface conditions of copper tubes are unchanged with respect to the rate of heat transfer.

#### Thickness of Layer

It was at first considered necessary to plate a very thick layer of nickel on the copper tube, and the initial experiments were made with a plating as thick as 2.5 mm. (0.1 inch). Later experiments showed that a layer one-fifth to one-tenth as thick was satisfactory, but even a layer of this thickness is quite difficult to put on smoothly. A much easier operation is the enclosure of copper wires in an electrolytic deposit of copper on the surface of a nickel tube, because a thick copper plate may be obtained without roughness. The plated deposit must be thick, preferably as thick as the diameter of the wires, in order that the heat conducted along the wires may be dissipated through a large mass of metal before the interface is reached, to prevent irregularities of temperature there. A thick layer introduces an error, however, because the temperature is measured, not on the outer surface of the tube in contact with the fluid, but at the interface between the plating and the tube proper. In accurate work correction may be made for this by means of the equation  $Q = \lambda S \Delta\theta / \Delta t$ , where  $Q$ , the quantity of heat flowing;  $\lambda$ , the coefficient of thermal conductivity of the metal in the plate;  $S$ , the area; and  $\Delta t$ , the thickness of the electroplate, are all known and the temperature correction,  $\Delta\theta$ , is to be calculated.

#### Preparation of Tube

The preparation of the tube for plating begins with a thorough cleaning with fine emery paper, wet pumice stone and a brush, hydrochloric acid, 10 per cent caustic solution, hydrochloric acid, and distilled water. The alkaline-acid treatments are repeated until a continuous film of water on the surface does not "break." After the mechanical and before the chemical treatment, the nickel wires for the thermocouple leads are attached. A piece of No. 30 nickel wire about 20 cm. (8 inches) longer than the circumference of the tube has the end bent back sharply to form a hook (Figure 1). The wire is wound once around the tube loosely and caught in the hook turned on the end. It is then caught with a pair of pliers at a point opposite the hook and a loop twisted until the wire holds tightly. The free end of the

wire, to which the lead wires will later be soldered or welded, is either given several coats of a rubber-base cement or, better, is entirely covered to its junction with the tube with a piece of small rubber tubing closed with cement. This is to prevent enlargement of the wires due to plating and must be carefully done because the solution plates through many ordinary insulations.

#### Plating

Two methods of plating were used—the first for 2.2-cm. ( $7/8$ -inch) tubes and the second for 7.6-cm. (3-inch) tubes. An anode was rolled out of sheet nickel to form a hollow cylinder about 7 cm. larger in diameter than the smaller tubes and a trifle longer than the part of the tube it was desired to plate. The tube was mounted concentrically with the anode in the plating solution. This method is applicable only for small tubes or for one on which only a small band is to be plated, because of the large anodes which would otherwise have to be employed. For the 7.6-cm. tube it was simpler to suspend it from a bearing and rotate it in the solution at about 100 r. p. m., in which was also immersed a standard rolled bar anode. The ends of the tube were closed with wooden plugs axially drilled for an iron rod which fitted tightly through them. A single heavy copper wire from the top of the tube to the vertical shaft served both as a flexible coupling and conductor of the plating current. The tube was filled with water to prevent its floating in the solution and was rotated smoothly by the motor driving the vertical shaft. The plating tank for a band more than 60 cm. (2 feet) long is most simply made by cementing together sections of standard sewer tiling.

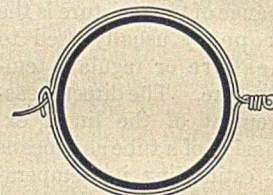


FIGURE 1.

The nickel-plating solution used was made up of 2.25 *N* nickel sulfate, 0.30 *N* boric acid, and 0.1 *N* nickel chloride. To this was added sufficient nickel carbonate to form a slight sludge, which was filtered off after boiling. The pH of the boiled solution was adjusted to 4.3 to 4.7 with sulfuric acid, and maintained in that range during the plating process by adding more sulfuric acid or nickel carbonate. One cubic centimeter of hydrogen peroxide was added per liter of solution per hour of plating time to prevent bubbles. A fixed brush held against a rotating tube or a periodic brushing of a stationary tube was found to keep the surface free from bubbles, but was not used except experimentally because of the mechanical difficulty presented by the attached wires. The solution was heated to about 40° C. before plating started, and the heat of reaction kept it at approximately that temperature throughout the process. If the solution cooled, a part was removed, heated, and returned. For the first tubes the current density was held at about 450 to 550 amperes per square meter of surface by a controlling rheostat, but in the case of the 7.6-cm. tube, which was to be plated for 1 meter of its length, the capacity of the generator limited the density to about a third of this value. When the plating was put on as thick as was possible without obtaining bubbles or excessive "tree" growths, the tube was removed from the solution and all "buds" filed off. The irregularities built up around the wires and their hooks and loops were filed until the whole tube had a smooth surface.

#### Description of Tubes and Temperature Measurements

Of the tubes which were prepared with thermocouples in this way, three will be described.

TUBE 1—The first (Figure 2) was a 2.2-cm. ( $7/8$ -inch) copper tube plated in a 2-liter graduate using a sheet-nickel



anode. It was rotated, and in 20 cm. of length near one end had nine wires embedded in a nickel plate about 2.5 mm. thick. Except for the 20 cm. to be plated, the tube was protected from electrodeposition by rubber tubing tied on tightly. After plating, the tube was placed in a lathe and a cut in the plating made between the third and fourth and between the sixth and seventh wires (Figure 2). This left three thermocouple wires on each of the three nickel bands. The ends of these wires were soldered to nickel wires leading to copper junctions which were immersed in melting ice. A single return for the other side of the circuit was made by winding a bright copper wire around the polished end of the copper tube and connecting this wire to the measuring instrument. In this, as in all other experiments, the thermocouple wires were insulated with small rubber tubing. The tube was then steam-jacketed (the copper lead wire was connected outside of the steam jacket) and a connection made

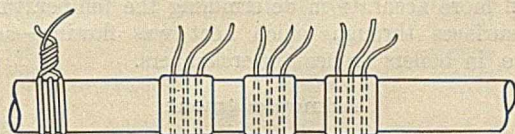


FIGURE 2.

to circulate cold water through it. Since it was possible to measure the inlet and outlet temperatures and the volume of this cooling water, a complete heat balance could be made.

*Note*—If the wires are to be exposed to steam for long periods of time, the sulfur in vulcanized rubber destroys them. Unvulcanized rubber tubing or varnished cotton tubing as is used in radio work may be used if the wires are otherwise uninsulated. Copper wires which are enameled and protected by double silk insulation have been uninjured when encased in vulcanized rubber tubing in steam for a period of several months.

Several average series of readings are reproduced with a temperature drop of 3 to 5 degrees from the steam to the tube. A larger temperature drop could not be obtained with this apparatus, but more heat was flowing per unit area than in the usual evaporator or condenser. 2.170 millivolts correspond to 100° C., and the millivolts corresponding to the temperature of the tube surface are shown for each thermocouple.

(Figures in millivolts)								
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
2.165	2.160	2.160	2.164	2.164	2.164	2.164	2.162	2.161
2.099	2.096	2.092	2.100	2.100	2.100	2.100	2.100	2.100
2.106	2.100	2.100	2.111	2.109	2.105	2.100	2.100	2.100
2.121	2.121	2.120	2.120	2.118	2.118	2.118	2.124	2.124
2.074	2.093	2.093	2.093	2.093	2.093	2.093	2.093	2.093

Each line of data represents conditions maintained as nearly constant as possible with this rough apparatus. In some cases the steam-film coefficient was calculated and the average of the values obtained was 3100 b. t. u. per square foot per degree Fahrenheit per hour, which is in good agreement with the work of other experimenters using other methods of temperature measure.

**TUBE 2**—The second tube (Figure 3) was 7.6 cm. (3 inches) outside diameter and was rotated while being plated as described above. Six wires were equidistantly spaced in the middle 75 cm. of its 125 cm. length. Except for about 12 cm. on each end, the tube was covered with a firm, smooth nickel layer approximately 0.25 mm. thick. The exact value was obtained from the difference of the averages of about 120 micrometer measurements before and the same number after plating. A thicker plate might have been better, but it was realized from the appearance of the tube that a rough surface would be obtained if the plating was continued. Experimentation in this field would probably make it possible to produce much thicker layers of electrodeposited nickel than have so far been obtained without surface roughness.

A channel about 6 mm. ( $\frac{1}{4}$  inch) in width and deep enough to expose the copper was cut entirely around the tube about 15 cm. from each end. This localized the central part of the tube (A, Figure 3) as the thermocouple surface, and eliminated temperature discrepancies due to end conduction. The single copper lead (B) to the potentiometer was attached to a copper screw so arranged that it could be screwed down tightly on the bare end of the copper tube. In addition to the nickel wires leading to copper wires in cold junctions, a copper wire was soldered to each nickel wire at a point (C) about 10 cm. from the attachment with the tube. Thus each of the six thermocouple circuits had three junctions—the junction on the tube surface, the junction about 10 cm. from the tube in the steam space, and the cold or ice junction. By combining any two of these three junctions in pairs it was possible to obtain three different temperature differences: that between the tube and the ice point—i. e., the temperature of the tube above 0° C.; that between the steam and the ice point—i. e., the temperature of the steam above 0° C.; and that between the steam and the tube—i. e., the "temperature drop" directly. Since this last temperature difference is small compared with the actual temperatures of the tube or the steam, and since in any apparatus for the study of heat transfer fluctuations of operating conditions, and hence temperature, are unavoidable, it is an advantage to be able to read the small temperature difference directly instead of finding it by subtraction of the tube temperature from that of the steam. This method eliminates the simultaneous readings of tube and steam temperatures which would otherwise be necessary.

The thermocouple wires were insulated and connected to a selective switchboard, which was in turn connected to a Leeds and Northrup type K potentiometer. The tube was fixed in its position in an apparatus for studying the rate of condensation of steam which will be described in another report. The thermocouples were calibrated and, except for one which had been damaged, were so consistent in their readings that they were connected in multiple and always read that way. Since a reading of e. m. f. on a potentiometer is independent of the resistance of the circuit, no corrections for the decreased resistance of the several thermocouple circuits in parallel, as compared with that of a single one, were

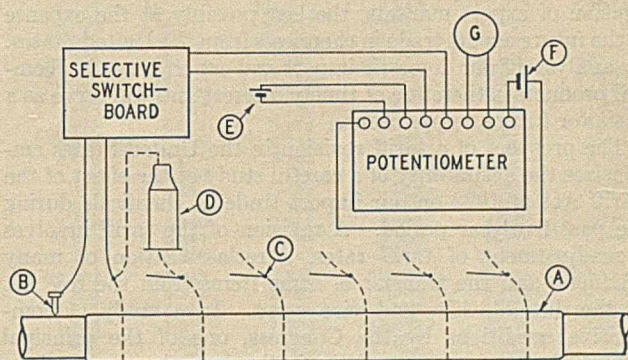


FIGURE 3.

necessary. This difference of resistance might cause an appreciable error if a low-resistance millivoltmeter were used to measure the thermal e. m. f.

**TUBE 3**—The third tube, which was plated, was a 2.2-cm. ( $\frac{7}{8}$ -inch) nickel tube 125 cm. long taken from a Swenson experimental evaporator. Four copper bands about 2 cm. wide and 1 mm. thick were electrodeposited at different distances along the length. Two No. 30 copper wires were embedded in each of two of the bands, and a single No. 30 copper wire was embedded in each of the other two. Rubber tubing prevented plating of the tube except on these bands.

A glass graduate was used as a plating tank, a cylindrical anode was used and the tube was not rotated. The solution was 1.6 *N* copper sulfate and 1.6 *N* sulfuric acid, and the deposit was thicker and smoother than the nickel deposits. Near one end of the tube a band of nickel enclosing two nickel wires was plated on, the wires forming the other side of the thermocouple circuit. After the usual external connections were made with the tube in position in the evaporator, the thermocouples were calibrated against a standard thermocouple. Water was circulated in the evaporator at various temperatures and the thermocouples checked among themselves to 0.03–0.05° C.

#### Discussion of Results

The agreement among the thermocouples attached to these three tubes was of the same order when there was a large temperature difference between the tube and the steam as it was when the tube and surroundings were in thermal equilibrium. Temperature differences of as high as 35° C. between tube and steam have been measured with these thermocouples, and the agreement between readings has always been within a millionth of a volt, corresponding to about 0.05° C., when it was possible to maintain uniform operating conditions during the reading of the thermocouples.

As has been mentioned above, a thicker and smoother electroplate could be deposited if the surface of the tube was

brushed during plating. A very thick plate of nickel (3 to 4 mm.) can be put on in this way in a hot solution with high current density if no wires are to be embedded. An arrangement of a nickel screw to be pressed or screwed against a point of the nickel surface could be devised which should answer the same purpose as the embedded wires. No experiments have been made with this type of junction, or with a junction formed by simply welding a nickel wire to a heavy nickel plate.

Because of the very high rate of heat transfer between a condensing vapor and a metal surface, the measurement of the temperature of a surface on which steam is condensing is more liable to errors than a similar temperature measurement of a surface through which heat is passing between two fluids without a change of state. It is therefore believed that this method, which has been successful in several studies in the condensation of steam during the last year, would be even more accurate in determining the temperatures of other surfaces through which heat was flowing—as, for example, in boilers or heat interchangers.

#### Acknowledgment

The authors wish to express their thanks to Prof. W. L. Badger of this department for his helpful supervision of the work, and to Prof. E. M. Baker for his assistance in the plating processes.

## Our Export and Import Trade in Chemicals<sup>1</sup>

### A Five-Year Review

Frank Talbot and W. N. Watson

WASHINGTON, D. C.

**P**UBLIC attention is at present focused on the recent international agreements among the cartels or consolidations in Europe, for the purpose of fixing prices, preventing overproduction, and for the division and expansion of export markets, the last possibly at the expense of the future export trade in chemicals from the United States. An analysis of our domestic import and export trade in chemical products is therefore of timely interest and will serve as a basis for future comparisons.

The prospect of a tariff revision in the United States emphasizes the desirability of a careful study of the effect of the Tariff Act of 1922 on our import trade in chemicals during the past five-year period. A revision of the tariff involves a readjustment of tariff rates, a reclassification of many products, and the transfer of some items from the free list to the dutiable list, and vice versa. In a study of competitive conditions by the Congress, one of the principal criteria for gaging competition is the imports of any given commodity. A review of our import and export trade, furthermore, reveals many significant changes resulting from the development of new chemical products which either serve as substitutes for some of those now in use or have found new and distinct uses.

In order to have a common basis for comparison, values must be taken rather than quantities, and a correction in value made according to changes in the index of commodity prices. Index numbers for chemical products, as published by the United States Bureau of Labor Statistics, are shown in Table I. The price base used in this table is 1926, as it

has become increasingly apparent that the year 1913 is now too remote to furnish a satisfactory base for comparing price levels in recent years.

Table I—Chemicals and Allied Products: Index Numbers of Wholesale Prices, by Groups of Commodities, 1914, 1922–1926

(Source: 1923–1926, Bureau of Labor Statistics; 1914, 1922, by calculation)

	1914	1922	1923	1924	1925	1926
Chemicals and drugs:						
Chemicals	85.1	95.6	100.6	102.2	104.1	100.0
Drugs and pharmaceuticals	58.3	87.4	95.7	95.8	97.7	100.0
Fertilizer materials	83.7	102.7	102.5	92.6	98.8	100.0
Mixed fertilizers	...	...	...	107.4	95.9	100.4
All chemicals and drugs	77.7	95.9	101.1	98.9	101.8	100.0
Paint materials	...	...	101.3	99.7	109.3	100.0

The index number of the wholesale prices of all commodities on the same base is as follows:

1914	64.0	1924	98.1
1922	97.3	1925	103.5
1923	100.6	1926	100.0

In the present article the statistics in general have been tabulated in accordance with the classification used by the Department of Commerce in "Foreign Commerce and Navigation of the United States," in 1926. As the classification in that publication has changed somewhat from year to year, it has been necessary to retabulate the data for each of the years prior to 1926 in order to give a uniform basis of comparison.

Chemicals and related products have been classified in three groups, as follows: Group A consists of coal-tar chemicals, medicinals, pharmaceutical preparations, and industrial chemicals. Group B includes allied products, such as paints,

<sup>1</sup> Received December 13, 1927.

fertilizers, explosives, soaps, perfumery, pyroxylin products, and polishes. In Group C will be found vegetable oils, essential oils, gums, botanical drugs, and dyeing and tanning materials and extracts.

### General Trend

In 1922 the imports of chemicals and related products (Groups A, B, and C) were valued at \$204,836,000, and in 1926 at \$262,382,000—an increase of 28 per cent. Exports of products in these three groups were valued at \$134,209,000 in 1922, and at \$174,283,000 in 1926—an increase of 30 per cent. Table II shows the value of imports and exports of products in Groups A, B, and C.

Table II—Chemicals and Related Products: Value of Imports and Exports, 1914, 1922–1926, and First Nine Months of 1927  
(000 omitted)

YEAR	IMPORTS	EXPORTS
1914 (fiscal)	\$159,321	\$ 86,867
1922	204,836	134,209
1923	242,550	151,933
1924	221,409	142,561
1925	257,647	163,059
1926	262,382	174,283
1927 (first 9 months)	201,385	136,776

Of the products in Groups A, B, C, imported in 1926, valued at \$262,382,000, a total of \$185,294,000, or 71 per cent, was imported free of duty, and \$77,088,000, or 29 per cent, was dutiable. Among the leading products imported in 1926 are sodium nitrate (\$42,781,386); coconut oil, a product of the Philippine Islands (\$22,087,870); dead or creosote oil (\$11,720,000); palm oil (\$10,111,588); and crude potassium chloride (muriate of potash) (\$6,195,830). Among the principal products exported in 1926 are gum rosin (\$21,903,780); ammonium sulfate (\$9,824,000); dyes (\$5,950,159); benzene (\$5,513,173); phosphate rock (\$4,435,590); carbon black (\$3,622,907); and caustic soda (\$3,111,510).

Imports of chemicals and allied products (Groups A and B) in the fiscal year 1914 were approximately double the value of exports in that year. In 1923, the first full calendar year

during which the act of 1922 was in effect, the values of domestic imports and exports of products in Groups A and B were practically identical. The annual value of imports during the period 1924–1926 has been slightly in excess of the value of exports. Imports of chemicals and allied products (Groups A and B) were valued at \$103,880,000 in 1914; \$97,717,000 in 1922; and \$137,570,000 in 1926. The value is about 33 per cent greater in 1926 than in 1914, but after making a correction according to the index of chemicals and drugs the value is approximately the same in 1926 as in 1914. Data presented in Table III indicate an increase of 52 per cent from 1922 to 1926 in the imports of chemicals and allied products (Groups A and B) entered free of duty and of 22 per cent in the value of dutiable products. Of the products in Group C the imports during the years 1923–1926, with the exception of 1924, were valued at approximately \$120,000,000 each year.

Data presented in Table IV indicate that Groups A and B had an export value of \$56,385,000 in 1914; \$105,788,000 in 1922; and \$132,373,000 in 1926. The value for each of the years 1922–1926 shows an increase over 1914, after making a correction according to the index of prices. During 1922–1926 there was an increase in exports each year, with the exception of 1924. The value of exports of products in Group C has increased each year during the five years ending with 1926 when exports were \$41,910,000.

### Group A

COAL-TAR CHEMICALS—Imports in 1914 of coal-tar chemicals (principally coal-tar dyes and other finished products) were valued at \$16,141,000. The value has increased since the passage of the act of 1922, while the character of the imports has undergone a notable change. In 1926 imports of coal-tar chemicals were valued at \$19,827,000, of which total coal-tar crudes were valued at \$13,069,000, and dyes and other finished products at \$6,007,000. The imports

Table III—Imports of Chemicals and Related Products, 1914, 1922–1926 and Nine Months of 1927  
(Compiled from "Foreign Commerce and Navigation of the United States," Department of Commerce)

	1914 (fiscal)	1922	1923	1924	1925	1926	1927 <sup>a</sup> (9 months)
Total groups A, B, and C	\$159,321	\$204,836	\$242,550	\$221,409	\$257,647	\$262,382	\$201,385
Chemicals and allied products (total Groups A and B)	103,880	97,717	121,908	121,506	139,936	137,570	99,264
Free		60,450	86,617	89,375	98,573	91,889	
Dutiable		37,267	35,291	32,131	41,363	45,681	
Group A—Chemicals (total)	50,315	37,365	45,866	42,661	48,212	54,020	43,620
Coal-tar chemicals (total)	16,141	10,986	16,983	19,712	20,249	19,827	17,707
Crudes		4,706	11,594	14,368	12,026	13,069	11,949
Intermediates		403	552	770	1,148	751	887
Dyes and other finished products		5,877	4,837	4,574	7,075	6,007	4,871
Medicinals and pharmaceutical preparations	6,306	5,636	5,219	4,704	5,648	5,891	4,031
Acids and acid anhydrides	1,457	1,668	3,665	3,202	3,010	2,497	2,597
Ammonium compounds (except fertilizers)	648	1,720	1,760	738	1,095	1,060	832
Barium compounds	441	536	383	412	362	307	175
Calcium compounds (acetate and chloride)	62	1,821	49	138	157	251	...
Potassium compounds (except fertilizers)	1,835	4,348	4,330	3,302	4,603	4,675	5,728
Sodium compounds (except fertilizers)	1,653	2,939	4,247	3,708	3,523	4,001	3,999
Other chemicals	21,772	7,711	9,230	6,745	9,565	14,562	9,151
Group B—Allied products (total)	53,565	60,352	76,042	78,845	91,724	83,550	55,644
Paints, pigments, varnishes (total)	2,341	3,652	3,317	2,841	3,208	3,822	2,828
Mineral pigments	615	1,314	1,331	1,088	1,210	1,534	1,216
Chemical pigments	1,074	1,705	1,512	1,302	1,432	1,466	1,063
Paints, stains, enamels	588	491	395	377	514	746	519
Varnishes	64	142	79	73	52	76	29
Fertilizer and fertilizer materials (total)	46,307	45,143	63,902	66,534	78,072	69,250	43,803
Nitrogenous	25,563	30,486	50,063	54,469	63,151	52,700	31,244
Phosphate	1,146	967	1,877	934	894	1,662	1,515
Potash	15,356	11,011	11,007	10,471	13,071	14,133	10,485
Other	4,242	2,679	955	660	956	755	560
Explosives, ammunition, pyrotechnics	847	992	872	1,006	1,142	1,119	953
Soaps	831	871	691	793	926	952	847
Perfumery, cosmetics, toilet preparations	2,607	8,973	5,523	5,870	6,277	5,420	5,129
Pyroxylin products (cellulose)	533	663	1,679	1,750	2,034	2,912	2,084
Blacking and polishes	49	58	58	51	65	75	...
Group C—Products other than chemicals and allied products (total)	55,441	107,119	120,642	99,903	117,711	124,812	102,121
Vegetable oils	29,111	58,708	63,613	59,261	74,229	78,483	64,248
Essential oils	3,017	5,413	5,638	5,462	6,356	6,504	4,886
Gums, resins, balsams <sup>b</sup>	8,493	22,755	33,744	21,305	21,308	23,798	18,333
Botanical drugs	9,291	7,937	8,721	7,879	7,639	8,170	6,429
Dyeing and tanning materials (crude)	2,299	7,673	3,929	2,963	3,760	3,819	3,775
Dyeing and tanning extracts	3,230	4,633	4,997	3,033	4,419	4,038	4,450

<sup>a</sup> General imports.

<sup>b</sup> Does not include rubber, turpentine products, camphor, or chicle.

Table IV—Exports of Chemicals and Related Products, 1914, 1922–1926, and Nine Months of 1927  
(Compiled from "Foreign Commerce and Navigation of the United States," Department of Commerce)

	(000 omitted)						
	1914 (fiscal)	1922	1923	1924	1925	1926	1927 (9 months)
Total Groups A, B, and C	\$86,867	\$134,209	\$151,933	\$142,561	\$163,059	\$174,283	\$136,776
Chemicals and allied products (total Groups A and B)	56,385	105,788	122,894	111,351	124,085	132,373	103,970
Group A—Chemicals (total)	22,118	51,006	56,472	52,867	57,558	62,937	53,175
Coal-tar chemicals (total)	...	7,622	12,332	9,976	10,761	14,095	13,299
Crudes	43	2,732	5,644	3,270	2,716	7,060	8,117
Intermediates	a	274	383	363	471	340	296
Dyes and other finished products	a	4,616	6,305	6,343	7,574	6,693	4,886
Medicinals and pharmaceutical preparations	6,722	14,195	16,177	17,441	19,768	19,677	14,800
Acids and acid anhydrides	483	1,447	1,036	959	981	1,005	685
Ammonium compounds (except fertilizer)	a	990	958	916	871	675	400
Calcium compounds	62,523	1,905	1,716	1,541	1,365	1,199	706
Potassium compounds (except fertilizer)	a	781	506	301	399	319	279
Sodium compounds (except fertilizer)	a	10,330	9,929	8,504	8,352	8,427	7,003
Other chemicals	12,347	13,736	13,818	13,229	15,061	17,542	16,003
Group B—Allied products (total)	34,267	54,782	66,422	58,484	66,527	69,436	50,795
Paints, pigments, varnishes (total)	7,256	11,479	14,552	14,326	18,510	18,888	15,727
Mineral pigments	} 5,121	973	999	824	903	1,006	839
Chemical pigments		4,327	7,667	5,898	7,680	7,984	6,458
Paints, stains, enamels		4,908	6,254	5,998	7,903	7,857	6,410
Varnishes		1,039	1,271	1,607	2,025	2,040	2,020
Fertilizer and fertilizer materials (total)	11,979	16,640	20,794	16,508	17,299	20,040	14,005
Nitrogenous	a	8,821	11,733	7,202	7,116	10,390	5,988
Phosphate	10,618	5,858	5,772	5,121	6,667	5,373	4,963
Other	62	1,961	2,389	4,186	3,516	4,277	3,054
Explosives, ammunition, pyrotechnics	6,272	6,910	7,680	7,416	8,420	7,943	5,270
Soaps	4,939	8,913	9,306	7,733	8,036	8,402	5,919
Perfumery, cosmetics, toilet preparations	1,621	6,310	6,879	7,252	8,083	8,404	6,766
Pyroxylin products	1,388	2,373	3,269	3,062	4,011	3,797	1,605
Blacking and polishes	812	2,157	1,942	2,187	2,168	1,962	1,503
Group C—Products other than chemicals and allied products (total)	30,482	28,421	29,039	31,210	38,974	41,910	32,806
Vegetable oils	15,624	14,114	10,593	9,454	12,554	9,320	8,368
Essential oils	628	884	1,012	1,675	1,673	1,695	1,551
Gums, resins (except rubber)	11,217	7,856	11,734	14,494	19,822	25,479	19,141
Botanical drugs	2,346	3,214	3,543	4,040	2,961	3,578	2,303
Dyeing and tanning materials (crude)	27	139	90	93	141	60	68
Dyeing and tanning extracts	640	2,214	2,067	1,840	1,798	1,779	1,375

a Not shown separately.

b Acetate and carbide only.

of coal-tar dyes in 1926 were equal to 11 per cent of the total United States production by value, and 5.3 per cent by quantity. Imported dyes are mainly high-priced vat dyes and specialties, the production of which is increasing each year in the United States. The largest single coal-tar product entering the United States in 1926 was dead oil or creosote oil, of which 87,518,544 gallons, valued at \$11,720,000, were imported. The use of dead oil in the treatment and preservation of wood has greatly increased the consumption of this product during the past few years, with a resultant increase in both production and imports.

In 1914 domestic exports of coal-tar products were negligible, but during 1922–1926 they have been increasingly large. Exports of dyes and finished coal-tar products in 1926 were valued at \$6,693,000, and crudes were valued at \$7,060,000. Indigo and sulfur black make up the bulk of the dyes exported; the remainder are largely tonnage direct dyes. A total of 143,527,826 pounds of benzene, valued at \$5,513,173, was exported. Imports of coal-tar products have exceeded exports during the past few years; however, the excess of imports over exports is now much less than in 1914.

### Medicinals

A large part of the medicinals and pharmaceutical preparations imported consists of products manufactured from natural raw materials not available in the United States. Imports of this group were larger in 1914 than in any of the years from 1922 to 1926. Quinine sulfate and other quinine derivatives, other alkaloids and salts, and menthol are important items imported. In 1926 menthol imports were valued at \$2,808,205 and comprised a large part of the imports of medicinals in that year. Medicinals and pharmaceutical preparations figure among our leading chemical exports. In 1914 exports were valued at \$6,722,000 and have increased from \$14,195,000 in 1922 to \$19,677,000 in 1926. The medicinals exported include in large part pharmaceutical preparations, such as trade-marked or patented products.

ACIDS AND ANHYDRIDES—Imports of acids and acid anhy-

drides have declined from \$3,665,000 in 1923 to \$2,497,000 in 1926, of which \$862,175 were entered free of duty and \$1,635,272 were dutiable. Imports of acetic acid (all grades) in 1926 were valued at \$522,137, and of arsenious acid (or white arsenic) at \$510,227. Tartaric, sulfuric, and formic acids were imported in fairly large quantities in 1926. Practically all imports of sulfuric acid were from Canada, while Germany supplied almost all of the formic acid and a large part of the tartaric acid. Exports of acids and anhydrides have declined slightly following the passage of the act of 1922, but the value of exports in each of these years is still about double that of 1914. Boric acid obtained from natural deposits in California is exported in large quantities, and in 1926 totaled 1,414,655 pounds, valued at \$125,777.

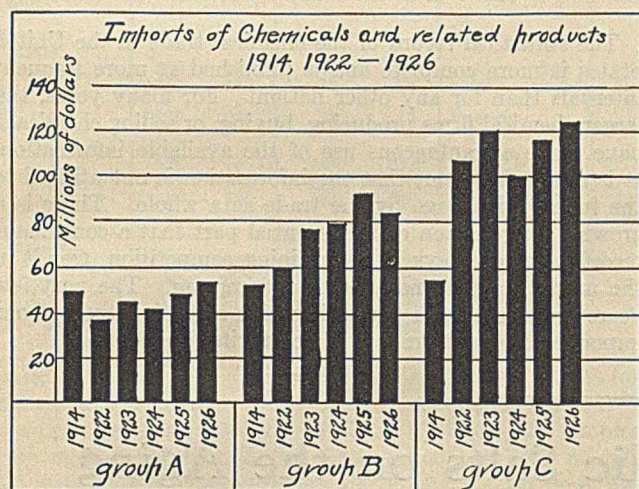
AMMONIUM COMPOUNDS—Imports of ammonium compounds in 1922 and 1923 were valued at over \$1,700,000 each year, but during 1924–1926 decreased on an average to slightly less than \$1,000,000 annually. Ammonium nitrate in 1923 totaled 19,919,016 pounds, valued at \$1,298,105, while in 1926 imports of this product had declined to 8,353,106 pounds, valued at \$383,405. Domestic imports of white and gray ammonium chloride in 1923 were valued at \$323,128, while in 1926 the value increased to \$613,482. Extensive demand for dry batteries for use in radio receiving sets has led to increased production and imports of ammonium chloride. Exports of ammonium compounds (not including ammonium sulfate) declined from \$990,000 in 1922 to \$675,000 in 1926.

POTASSIUM COMPOUNDS—Imports of potassium compounds (except fertilizers) during 1922–1926 totaled over \$4,000,000 each year. In 1926 imports of these products were valued at \$4,765,000, of which \$562,923 were free of duty and \$4,202,533 were dutiable. Included in the imports during 1926 was crude or partly refined bitartrate (argols) valued at \$1,779,943, coming largely from France. This product is used as the raw material in the manufacture of cream of tartar and tartaric acid, which, in turn, are used as ingredients of certain baking powders. Caustic potash valued at \$770,468, crude potassium nitrate at \$526,573, and potassium car-

bonate at \$533,840, were also included in the 1926 imports of this group.

**SODIUM COMPOUNDS**—Imports of sodium compounds in 1926 were valued at \$4,001,000. The principal item in this class was sodium cyanide, with a value of \$2,558,000, of which Canada supplied 24,297,245 pounds, valued at \$1,585,340. In 1926 exports amounted to \$8,427,000, including chiefly caustic soda valued at \$3,112,000, borax at \$1,256,798, and soda ash at \$936,000. The value of the domestic exports of sodium compounds (except fertilizers) during the years following the passage of the act of 1922 has been about double that of the imports.

**OTHER CHEMICALS**—Many chemicals imported or exported in large quantities are included in this classification. Imports of crude and refined glycerol in 1926, for example, were valued at over \$6,000,000, and imports of crude iodine were valued at \$2,272,343. Another chemical import of



interest was 169 grains of radium salts valued at \$548,788. Exports of other chemicals in 1926 were valued at \$17,542,000. Included in these were disinfectants valued at \$2,721,990, and baking powder—a distinctly American product—exports of which amounted to 4,500,523 pounds, valued at \$1,634,452. British South Africa in 1926 received the largest shipments of baking powder—658,216 pounds, valued at \$333,565.

**METHANOL**—An analysis of the import and export trade in chemicals during the past few years would be incomplete without some discussion of the remarkable change in the United States trade in methanol. In April, 1924, the Badische Anilin und Soda Fabrik announced the production of synthetic methanol at Ludwigshafen, and in 1925 imports of this material appeared in this country in considerable amounts. Prior to 1925 imports of methanol were unimportant. In that year, however, imports exceeded exports. The imports of methanol in 1926 were 754,917 gallons, valued at \$345,530, and the exports of pure and denaturing grades were 417,265 gallons, valued at \$311,508.

The import duty on methanol was increased by presidential proclamation from 12 to 18 cents per gallon, effective December 27, 1926, after an investigation by the United States Tariff Commission. During 1927 two domestic manufacturers began the production of synthetic methanol. During the first nine months of 1927 imports of synthetic methanol were 1,455,541 gallons, valued at \$635,573. During this same period exports were 165,296 gallons, valued at \$160,587. It is expected that the wood-chemical industry in the United States will meet increasing competition, not only from synthetic methanol, but also from acetone produced by the fermentation of corn and from synthetic acetic acid.

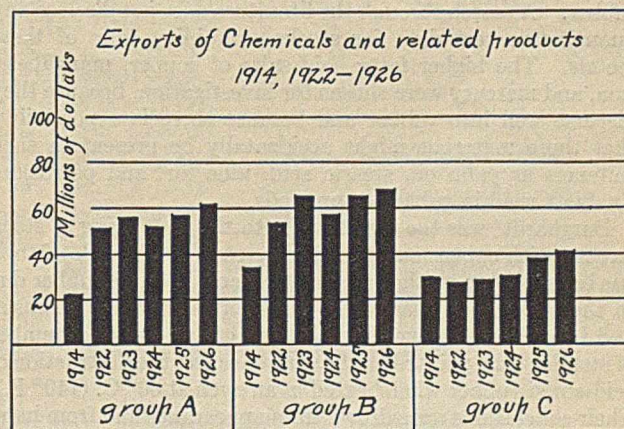
## Group B

**PAINTS, PIGMENTS, AND VARNISHES**—Exports of paints, pigments, and varnishes have been increasing during the past few years and their value is many times the value of imports. Imports of mineral and chemical pigments in recent years were valued at \$2,000,000 to \$3,000,000 while paints, stains, enamels, and varnishes were valued at less than \$1,000,000. On the other hand, exports of paints, stains, enamels, and varnishes have been valued at about \$10,000,000 during each of the years 1925 and 1926. The increasing popularity of nitrocellulose lacquers accounts for some of the increased export of these products. The United States does not export mineral pigments to any great extent, but the export of chemical pigments amounts to several millions of dollars. Carbon black produced from natural gas is the chemical pigment showing the largest export—39,210,389 pounds, valued at \$3,622,907, in 1926.

**FERTILIZER AND FERTILIZER MATERIALS**—Fertilizer and fertilizer materials are imported free of duty, with the exception of ammonium sulfate, which is dutiable at \$5.60 per ton. In 1926, of a total of \$137,660,000 of chemicals and allied products (Groups A and B) imported, more than half, or \$69,250,000, was fertilizer and fertilizer materials. In that year imports of nitrogenous fertilizers were valued at \$52,700,000 and potash fertilizers at \$14,133,000. Sodium nitrate (\$42,781,000) formed the bulk of the nitrogenous fertilizers imported. In 1926, 16,245 tons of ammonium sulfate nitrate known as Leuna saltpeter, valued at \$1,099,313, were imported. This is a new fertilizer material of considerable interest developed in Germany. It is imported free of duty, although ammonium sulfate and ammonium nitrate are separately dutiable. Of \$20,040,000 worth of fertilizers exported in 1926, ammonium sulfate alone made up nearly one-half, valued at \$9,824,000. Exports of phosphate rock have declined in recent years because of increased competition from African phosphate in European markets.

**EXPLOSIVES**—Imports of explosives, ammunition, and pyrotechnics have averaged about \$1,000,000 each year since 1922, while exports usually average several million dollars each year. In 1926 the United States exports of dynamite were 16,221,096 pounds, valued at \$2,330,533.

**SOAPS AND PERFUMES**—Imports of soaps average less than \$1,000,000 a year, but exports since 1922 have averaged between \$8,000,000 and \$9,000,000 a year.



The United States has a considerable import and export trade in perfumery, cosmetics, and toilet preparations. In 1914 imports greatly exceeded exports, but in recent years there has been an excess of exports. The Tariff Act of 1922 imposed a duty of 75 per cent ad valorem and 40 cents per pound on products of this group if containing alcohol, and

75 per cent ad valorem if not containing alcohol. While the imports of finished products have not increased under this act there has been an increase in the imports of semifinished perfumes or mixtures by branch houses of foreign manufacturers.

### Group C

**VEGETABLE OILS**—Exports of vegetable oils have declined in recent years, while imports have increased each year during 1922–1926 with the exception of 1924. Imports of vegetable oils in 1914 were about twice the value of exports. The value of exports in 1926 was \$9,320,000, a decline of over \$6,000,000 from 1914, while imports increased from about \$29,000,000 in 1914 to \$78,483,000 in 1926.

Cottonseed oil is the leading oil exported from this country. In 1926 the value of the crude cottonseed oil exported was \$2,486,102 and the refined \$1,603,549.

During 1922 to 1926 the increase in imports has been almost entirely in oils free of duty. In 1922, for example, imports of dutiable vegetable oils were valued at \$27,113,000, and in 1926 at \$20,824,000. Of the dutiable oils imported in 1926 edible olive oil was valued at \$14,411,530, rape oil \$2,025,034, and soy-bean oil \$1,877,864. Imports of duty-free oils, on the other hand, were \$31,596,000 in 1922 and \$57,659,000 in 1926. Of the leading oils imported free of duty in 1926, coconut oil from the Philippines was valued at \$22,087,870; palm oil, at \$10,111,588; and Chinese wood oil at \$9,148,090.

**ESSENTIAL OILS**—Imports of essential oils in 1926 were about double those for 1914. During 1922–1926 there was an increase in imports each year with the exception of 1924. In 1923, the first year of operation under the 1922 tariff act,

imports of essential oils entered free of duty were valued at \$4,163,310 and dutiable oils at \$1,474,714. In 1926, imports of duty-free oils were \$4,285,260 and dutiable oils, \$2,218,413. Among the dutiable oils showing a considerable increase in value of imports are lemon and orange oils, while imports of sandalwood oil show a large decrease. Peppermint oil forms a large part of the domestic exports of essential oils.

**GUMS, RESINS, AND BALSAMS**—Imports and exports of gums, resins, and balsams have increased considerably in 1926 over 1914. In 1926 imports of shellac (\$10,515,000) and other varnish gums, such as lac and copal, account for a large part of the total. Of the exports in 1926, gum rosin, valued at \$21,903,780, amounts to nearly 90 per cent, of which Germany and the United Kingdom are the principal consumers.

### Value of Record of Chemical Trade

The statistical record of the chemical trade in the United States is more complete and is published at more frequent intervals than for any other nation. For many years, the larger chemical firms producing, buying, or selling chemicals, have made advantageous use of the available information. It is a fact, however, that the information is not utilized to the fullest advantage by the trade as a whole. There is a growing appreciation of the essential part that a continuous record of trade plays in determining competition, trends of the market, and a manufacturing program. The next few years promise to be a period in which a careful study of our import and export trade will be of vital importance.

## Effect of Certain Metallic Salts on the Aging of a Tread Compound<sup>1</sup>

Bert S. Taylor and Webster N. Jones

THE B. F. GOODRICH COMPANY, AKRON, OHIO

**A**MONG rubber technologists it is generally accepted that certain metallic salts, such as those of manganese and copper, are deleterious to the aging of vulcanized rubber. A search through the literature does not disclose any quantitative test data for stocks containing salts of these metals. The higher fatty acid salts of copper, manganese, iron, and mercury were chosen for investigation, because they disperse well into rubber and because there is a possibility that these materials might accidentally be present in such softeners as palm oil, stearic acid, pine tar, and petroleum products used in rubber compounds.

Burghardt<sup>2</sup> was the first to refer to the poor aging of stock treated with copper oxide in the presence of olive oil. Much has been written on the cause of tackiness in crude rubber due to the presence of manganese<sup>3</sup> and copper salts.<sup>4</sup> Thomson and Lewis<sup>5</sup> have shown that solutions of any one of a number of metallic salts painted on the surface causes the destruction of acid-cured rubber when heated in an oven at 60° C. (140° F.). Their conclusions were drawn from appearance and from hand tests. Salts of the four metals considered—iron, copper,

mercury, and manganese—have all been used as catalysts of either oxidation or reduction in various media and under various conditions. All these metals form at least two oxides. Mackey and Ingle<sup>6</sup> have shown that the soaps of these metals and various others serve as driers in oils. This is claimed to be due to intermediate peroxide formation. Such peroxides, if formed in rubber compounds, might have a marked influence on their aging qualities.

### Procedure

In order to avoid variability in milling, portions of a 200-pound batch of the basic tread stock, mixed on a large mill, were blended on a laboratory mill with the proper amount of master batches of the various salts consisting of 90 per cent basic stock and 10 per cent of the salt in each case.

### Composition of Tread Stock

	Per cent
Rubber	60.0
Sulfur	2.5
Zinc oxide	5.0
Gas black	25.0
Softeners	7.0
Accelerators	0.5
	100.0

Since this same large batch was used for both of the master batches of the metallic salts and the test stocks, there was

<sup>6</sup> *J. Soc. Chem. Ind.*, 36, 317 (1917).

<sup>1</sup> Presented before the Division of Rubber Chemistry at the 74th Meeting of the American Chemical Society, Detroit, Mich., September 5 to 10, 1927.

<sup>2</sup> *India Rubber J.*, 5, 169 (1889).

<sup>3</sup> Bruni and Pellizola, *Giorn. chim. ind. applicata*, 3, 451 (1921).

<sup>4</sup> Van Rossem and Dekker, *Ind. Eng. Chem.*, 18, 1152 (1926).

<sup>5</sup> *India Rubber J.*, 7, 328 (1891).

**Data on Metallic Salts in Stock**  
Press cure, 45 minutes at 149° C. (300° F.). Tensile in kg. per sq. cm.; elongations in per cent

SALT IN STOCK	BIERER BOMB TEST <sup>a</sup>								GEER OVEN TEST <sup>b</sup>						APPEARANCE AND FEEL AFTER BOMB TEST
	TIME IN BOMB								TIME IN OVEN						
	Original		48 hours		96 hours		144 hours		5 days		9 days		14 days		
	Tens.	Elong.	Tens.	Elong.	Tens.	Elong.	Tens.	Elong.	Tens.	Elong.	Tens.	Elong.	Tens.	Elong.	
Blank	259	677	172	583	79	376	50	307	211	600	182	570	98	392	Remains soft
Cupric stearate:															
0.001	249	683	110	423	57	288	43	218	174	457	123	397	88	255	Same as blank
0.005	249	685	128	535	44	307	55	328	175	547	131	475	90	345	Same as blank
0.01	237	690	115	510	48	332	39	248	168	500	135	492	92	350	Same as blank
0.05	265	685	59	325	32	120	44	93	170	427	110	367	81	270	Same as blank
0.1	256	709	47	339	48	9			177	565	91	325	91	340	Brittle
0.2	247	685	23	0					174	540	86	333	84	310	Brittle
0.5	255	673							179	552	87	325	84	320	Brittle
Blank painted with CuCl <sub>2</sub> soln.	259	677	123	505	34	230	22	185	205	580	169	528	131	435	Brittle after 144 hours
Manganic oleate:															
0.1	256	665	67	368	41	288	34	205	181	545	143	470	111	407	Brittle
0.5	251	682	32	78	20	0			138	490	106	413	97	378	Brittle
1.0	236	653	13	10					111	455	84	362	66	303	Brittle
Ferric stearate:															
0.1	257	709	146	555	65	385	41	224	181	583	89	368	81	357	Same as blank
0.2	252	688	137	570	58	328	41	231	165	533	79	293	75	287	Same as blank
0.5	248	665	73	413	42	264			124	527	99	357	61	225	Brittle
Mercuric stearate:															
0.1	261	638	122	463	67	338	47	240	208	546	169	538	122	438	Same as blank
0.5	260	627	131	498	71	355	46	230	212	545	166	517	134	418	Same as blank
1.0	267	653	117	453	65	293	48	228	219	567	174	545	128	420	Same as blank

<sup>a</sup> At 70° C. and 20 atmospheres oxygen. <sup>b</sup> At 70° C.

no difference between one test recipe and another except for the amount of metallic salt added. The samples were cured in a press for 45 minutes at 149° C. (300° F.). The samples were aged in a Bierer-Davis oxygen bomb at 300 pounds (20 atmospheres) pressure and 70° C. for 48, 96, and 144 hours. They were also aged in the Geer oven at 70° C. for 5, 9, and 14 days. A badly aged piece of stock containing copper or manganese salts from the bomb was hard and stiff, while the strips from the oven were merely weakened, with relatively little change in flexibility. (See Figures 1 and 2.)

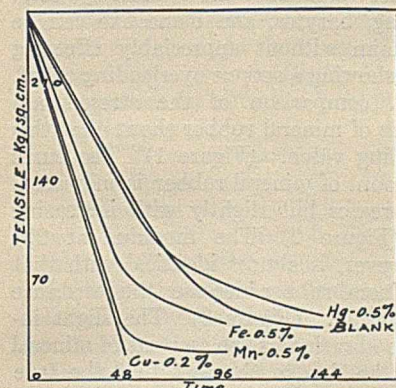


Figure 1—Change in Tensile in Aging Bomb at 70° C. Due to Presence of Metallic Salts

further deterioration in this type of test.<sup>7</sup>

The data are given in the accompanying table.

#### Summary

1—The effect on aging produced by the addition of low concentrations of iron, copper, manganese, and mercury salts of higher aliphatic organic acids to a tread compound was investigated.

2—The data obtained from aging in the bomb show that the presence of copper and manganese salts of organic acids in very small concentrations is harmful to the aging of rubber.

<sup>7</sup> Williams, *Ind. Eng. Chem.*, 18, 369 (1926).

As little as 0.1 per cent of either cupric stearate or manganic oleate is detrimental. Iron stearate has a less deleterious effect, but 0.5 per cent iron stearate produced much poorer aging than the blank. The mercury salts in the concentrations used—0.1 to 1.0 per cent—did not affect the aging so noticeably as the other salts.

3—The effects of aging in the Bierer-Davis bomb and in the Geer oven are markedly different, both as to tensile strength and the hardening of the test strips. The bomb test at 70° C. was much more severe than the oven test at the same temperature. Further investigation will be made to determine which type of artificial aging test most nearly corresponds to the natural aging of these stocks.

4—The presence of copper chloride on the surface of the test strips exerts a deteriorating influence on the stock in the aging bomb. The effect is similar to that obtained when copper stearate is compounded into the stock.

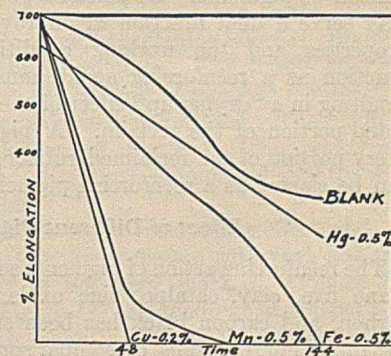


Figure 2—Change in Elongation in Aging Bomb at 70° C. Due to Presence of Metallic Salts

## Calendar of Meetings

American Ceramic Society—30th Annual Meeting, Hotel Ambassador, Atlantic City, N. J., February 5 to 11, 1928.

American Chemical Society—75th Meeting, St. Louis, Mo., April 16 to 20, 1928.

Institute of Chemistry—Northwestern University, Evanston, Ill., July 23 to August 18, 1928.

American Electrochemical Society—Hotel Stratfield, Bridgeport, Conn., April 26 to 28, 1928.

# RECLAIM SYMPOSIUM

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## Pigment Reënforcement of Reclaimed Rubber

H. A. Winkelmann and E. G. Croakman

THE PHILADELPHIA RUBBER WORKS COMPANY, AKRON, OHIO

COMPOUNDING ingredients of many types are in use in rubber compounds and, although their effect on rubber has been extensively investigated, there has been very little work published to show their effect on reclaim alone. The behavior of reclaimed rubber in compounds which also contain crude rubber, accelerators, and pigments is well known. The presence of these variables makes it impossible to determine the effect of the pigment on the reclaim itself. In this study we propose to show (1) the effect of varying volume loadings of different pigments on a whole-tire reclaim cured with sulfur, (2) the effect of accelerators and activators, and (3) the effect of curing at lower temperatures. With crude rubber the desired physical properties may often be obtained by cure or by the combined effect of cure and the reënforcing action of compounding ingredients. Owing to the degree of disaggregation of the reclaimed rubber the effect of cure is greatly decreased and the action of reënforcing pigments is necessary to bring out the maximum physical properties of the reclaim. The soluble and insoluble phases of reclaimed rubber differ in chemical and physical properties, indicating varying degrees of disaggregation of the rubber hydrocarbon.

Reclaimed rubber affords a very good medium for the dispersion of pigments. Dispersions of pigments in a reclaim may serve a dual function in improving both the physical properties and the working conditions. A pigment, to function as a reënforcing agent, must absorb the rubber, resulting in a "drying up" effect of the more highly disaggregated portion of the reclaim. A pigment must reënforce every portion of the reclaimed rubber hydrocarbon before it can be classed as a reënforcing pigment.

### Effect of Different Pigments

The reënforcing action of pigments such as whiting, barytes, blanc fixe, clay, catalpo, zinc oxide, Kadox, thermatomic carbon, and carbon black has been studied in a whole-tire reclaim. For purposes of comparison a standard grade of mineral rubber was also used. The whole-tire reclaim used had a rubber value of 57 per cent. The same lot of reclaimed rubber was used throughout. Varying volumes of each pigment—viz., 2.5, 5, 10, 15, and 20—were added to 100 volumes of the reclaim and cured with 5 parts of sulfur. This volume-loading range insures both a minimum and a maximum loading effect. Each compound was cured for lengths of time varying from 15 to 55 minutes at 287° F. (141.7° C.). The reënforcing action of each pigment on the reclaim and the rubber hydrocarbon in the reclaim was thus observed without the presence of other factors.

Stress-strain, tensile strength, elongation, permanent set, resistance to tear, resistance to abrasion, and plasticity measurements have been made in order to correlate the effect of these pigments on each of the above factors. The abrasion tests were made on the New Jersey Zinc Company's abrasion machine.

Two methods of mixing were used to insure the best dispersion possible and to serve as a check throughout the work. In one series of experiments the pigments were added to the unfinished reclaim and then refined; the sulfur was then added. In the second series the pigments and sulfur were added to the finished reclaim on the mixing mill. Owing to the close agreement of the results obtained by the two methods only the experiments in which the pigments were refined into the reclaim will be reported. Refining versus mixing did not show marked differences in physical properties of the 5- to 10-pound batches which were used. In general, when the pigment was refined into the reclaim a higher elongation was obtained, although the tensile strength was not always increased. The refining of pigments and reclaim in factory practice gives better dispersion due to breaking up of pigment agglomerates. The results are improved physical properties and a smoother reclaim, depending upon the pigment used.

A study of the physical properties of the compounds containing various pigments shows that carbon black is the only pigment that has a marked reënforcing effect with increasing volume of pigment. Twenty volumes of carbon black still show an improvement in the physical properties. Thermatomic carbon, clays, and zinc oxides show some effect, whereas the other pigments show scarcely any. Large amounts of whiting, barytes, and blanc fixe can be compounded into a reclaim without appreciably affecting the stress-strain curve or showing a serious overloading effect.

MINERAL RUBBER—A comparison of the stress-strain curves of varying volumes of mineral rubber shows that this material has no reënforcing value. (Figure 1) The cures become softer as the amount of mineral rubber is increased. The tensile strength decreases but slightly with increasing volumes of pigment. (Figure 2) The modulus at 200 per cent elongation, however, is almost identical with that of the reclaim alone. Mineral rubber increases the resistance both to tear and to abrasion. (Figure 3) The slight increase in the resistance to abrasion as the amount of mineral rubber is increased may be due to the fact that the true abrasion loss is not obtained because the stock becomes soft.

WHITING—The stress-strain curves of varying volumes of whiting show that it is almost inert as a reënforcing pigment. (Figure 4) There is only a slight stiffening shown in the lower part of the stress-strain curve. The tensile strength decreases with increasing volumes of whiting. (Figure 2) The elongations at break and modulus at 200 per cent elongation are identical with the blank. The resistance to tear (Figure 3) is increased slightly with 10 volumes of whiting, while the resistance to abrasion increases up to 10 volumes and then remains constant.

BARYTES—This pigment shows no reënforcing effect with increasing volumes of pigment. (Figure 5) Even with 20 volumes no stiffening is indicated and lower tensiles



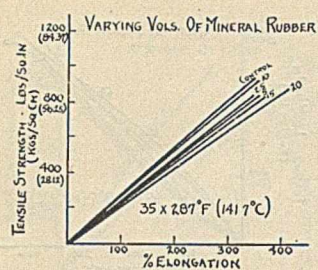


Figure 1

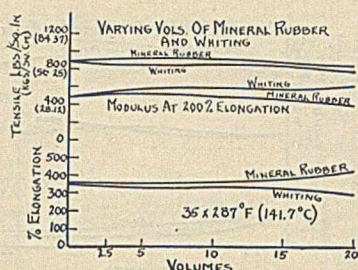


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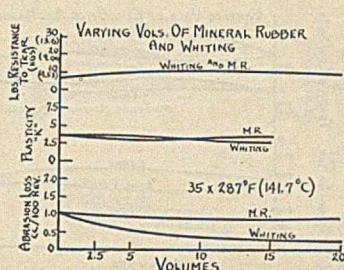


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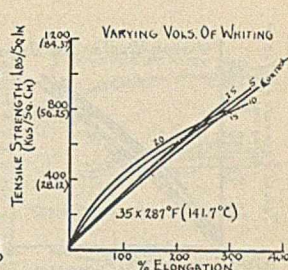


Figure 4

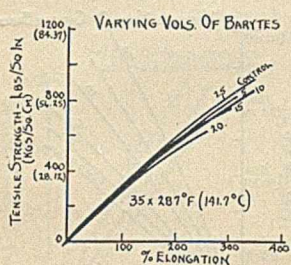


Figure 5

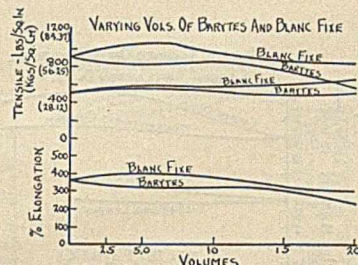


Figure 6

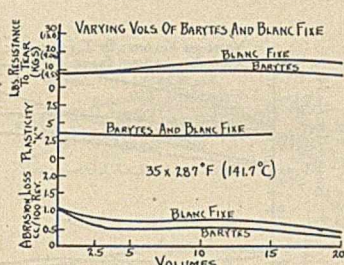


Figure 7

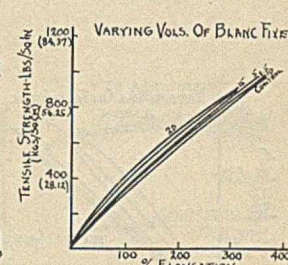


Figure 8

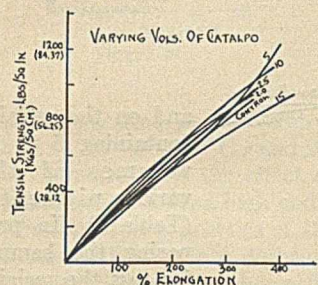


Figure 9

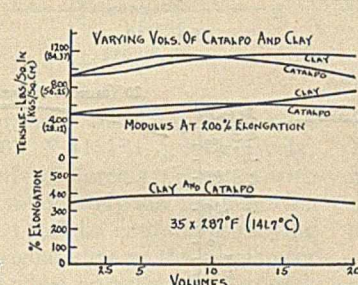


Figure 10

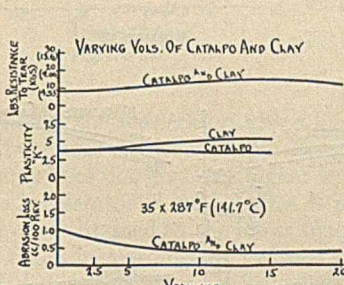


Figure 11

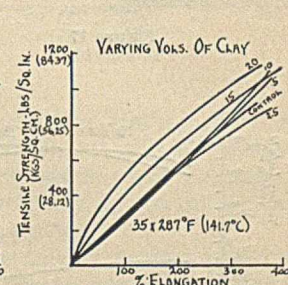


Figure 12

are obtained in each case. Barytes results in a gradual decrease in the tensile properties with increased volume loading while the modulus at 200 per cent remains almost constant. (Figure 6) A slight lowering of the elongations occurs. The resistance to tear (Figure 7) is not affected, although the resistance to abrasion is improved with each addition of pigment.

BLANC FIXE—A maximum reënforcing effect is shown with 20 volumes. (Figure 8) Its effect is very slight, however, and shows but very little improvement over the reclaim alone. Increased volume loading gives higher tensiles to 5 volumes, after which there is a decrease due to overloading. (Figure 6) A slight decrease in the elongations is also obtained. Better resistance to tear and abrasion (Figure 7) are obtained than with the reclaim alone.

CATALPO—There is a reënforcing effect without any stiffening action. (Figure 9) Higher elongations are obtained with catalpo than with the reclaim itself, showing that a further plasticizing effect may have taken place as a result of the working in of the pigment. Both the resistance to tear and to abrasion is superior to that obtained with the reclaim. A higher permanent set is observed over the full range of cures. Increased volume loading (Figure 10) gives a slight increase in tensile up to 10 volumes, after which it decreases again, while the elongation remains almost constant. Practically no effect is produced on the modulus at 200 per cent elongation. The resistance to tear (Figure 11) is only slightly increased, although the resistance to abrasion is appreciably improved with each additional amount of pigment.

CLAY—A stiffening as well as a reënforcing action is

shown. (Figure 12) The stress-strain curve with 2.5 volumes is lower than the reclaim alone, but as the amount of pigment is increased a decided stiffening effect is obtained, reaching a maximum of 20 volumes. The tensile strength (Figure 10) improves as the amount of pigment is increased, while the elongations remain almost constant. The modulus increase with each addition of pigment. The resistances to tear (Figure 11) and abrasion are increased slightly with increased volume loading.

ZINC OXIDE—Zinc oxide has a reënforcing effect and, although the degree of stiffening increases with each addition of pigment, this effect is not very marked. (Figure 13) The tensile strength (Figure 14) and modulus at 200 per cent increase slightly with each addition of pigment. The elongation, however, remains practically constant even up to 20 volumes. The resistances to tear and abrasion increase slightly. (Figure 15)

KADOX—There is a decided reënforcing effect and in every instance the ultimate breaks are higher than those obtained with the reclaim alone. (Figure 16) Increased volume loading has little effect on the tensile strength (Figure 14) beyond 5 volumes, although there is an appreciable increase up to this point. The modulus at 200 per cent remains almost constant up to 20 volumes. Very little effect on the elongations is observed. The resistance to tear (Figure 15) and abrasion increases with each addition of Kadox and, in every case, is better than that obtained with the reclaim.

THERMATOMIC CARBON—The stress-strain curves with varying volumes of thermatomic carbon show decided reënforcing effect in reclaimed rubber. (Figure 17) The degree of stiffening is proportional to the amount of pigment added.

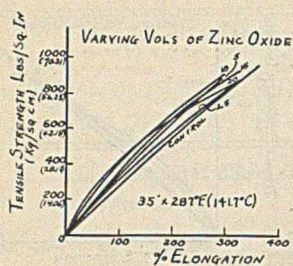


Figure 13

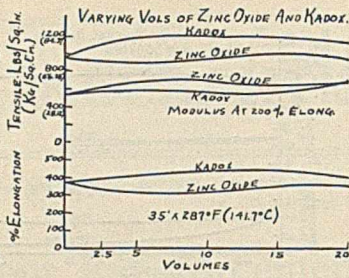


Figure 14

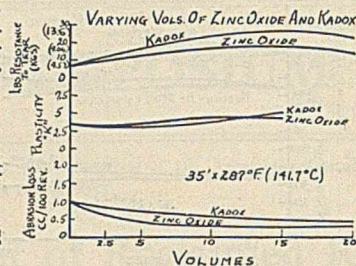


Figure 15

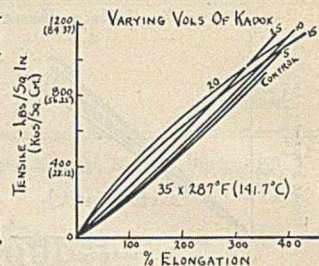


Figure 16

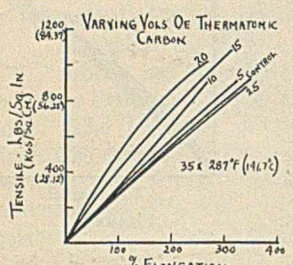


Figure 17

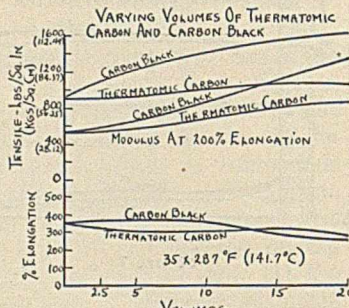


Figure 18

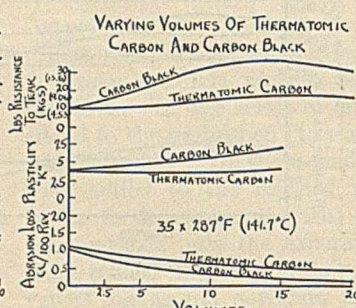


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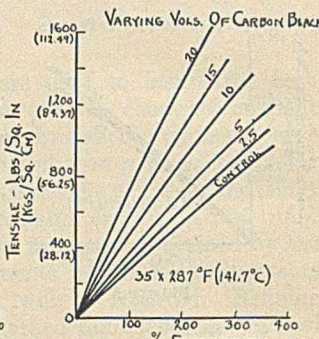


Figure 20

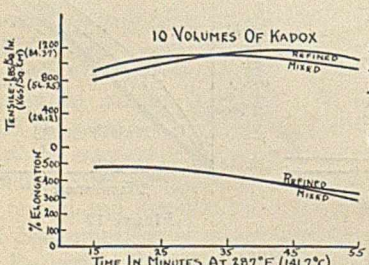


Figure 21

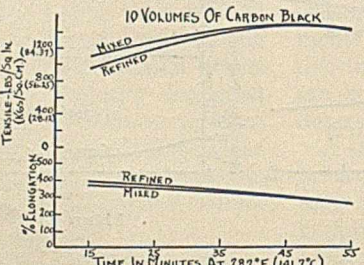


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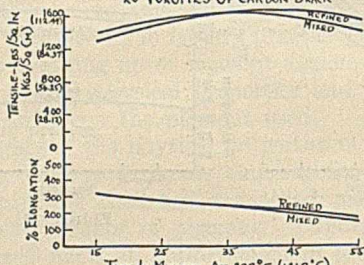


Figure 23

Increased volume loading (Figure 18) gives only a slight improvement in tensile strength and the effect on the elongation is almost negligible. The modulus at 200 per cent elongation and the resistance to tear (Figure 19) and abrasion increase with each addition of pigment.

**CARBON BLACK**—This material gives higher physical properties in every instance than the reclaim alone or any of the other compounding ingredients. (Figure 20) The reënforcing effect increases in proportion to the amount added. The tensile strength (Figure 18) increases with each addition of carbon black. With none of the other pigments does the modulus at 200 per cent elongation show such a marked increase with each addition of pigment. The resistances to tear (Figure 19) and abrasion are very much higher than those obtained with any other pigment.

Table I—Plasticity Measurements

ADDED PIGMENT	5 VOLUMES		15 VOLUMES	
	N value	Plasticity K	N value	Plasticity K
Mineral rubber	0.746	2.72	0.643	3.06
Whiting	0.521	3.91	0.569	3.84
Blanc fixe	0.747	3.69	0.569	3.84
Barytes	0.711	3.32	0.637	3.66
Clay	0.581	4.18	0.863	5.63
Catalpo	0.813	4.21	0.721	4.13
Zinc oxide	0.659	3.55	0.829	4.60
Kadox	0.668	3.32	0.531	4.76
Thermatomic carbon	0.963	3.38	0.718	3.53
Carbon black	0.663	4.09	0.527	6.36

Reclaim (no pigment)

N value 0.680 Plasticity K 3.53

**PLASTICITY**—Plasticity measurements were made on the Williams plastometer on the sample of reclaimed rubber

and on the reclaim containing 5 to 15 volumes of the various pigments. (Table I) In preparing the sample for test the reclaim is warmed by several passes through a cold mill with a setting of  $\frac{3}{16}$  inch (5 mm.). The

warmed stock is calendered as thinly as possible and is plied up to a thickness of about 14 mm. The plies are firmly pressed together to exclude air. A pellet having a volume of 2 cc. is used for each determination.

The mixtures containing mineral rubber have higher plasticity than the reclaim itself. Five volumes of barytes and thermatomic carbon give higher plasticity than the reclaim itself, but with 15 volumes the results are practically the same as with the reclaim alone. Five volumes of whiting, catalpo, and zinc oxide decrease the plasticity of the reclaim, although the addition of 15 volumes causes no further decrease. Clay, Kadox, and carbon black show a marked decrease in plasticity with increased volume loading.

The plastometer measures the resistance to flow at a given temperature and load. It does not measure the nerve or working properties of a rubber compound. It is possible for a rubber compound to show a high plasticity and yet have poor working properties due to nerviness.

**METHODS OF MIXING**—A comparison of the two methods of mixing which were used is illustrated in Figures 21, 22, and 23 for Kadox and carbon black. The tensile and elongation in each case check well within experimental error.

**Effect of Accelerators**

The effect of accelerators and an activator such as zinc oxide on the physical properties of a whole-tire reclaim containing varying volumes of whiting, clay, Kadox, and carbon black was determined. Diphenylguanidine and

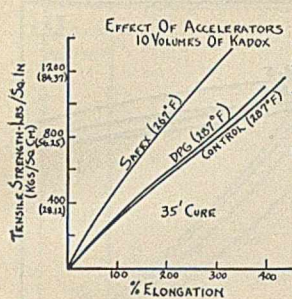


Figure 24

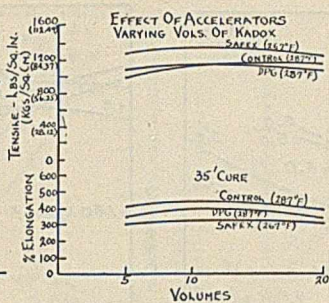


Figure 25

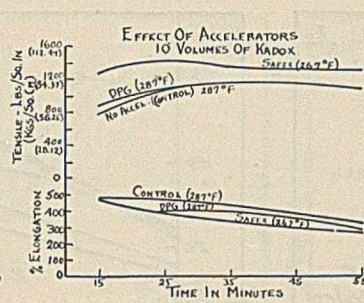


Figure 26

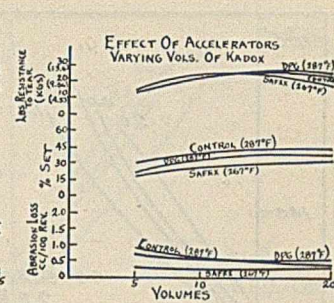


Figure 27

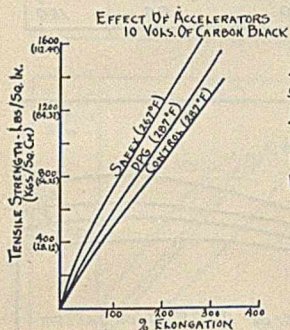


Figure 28

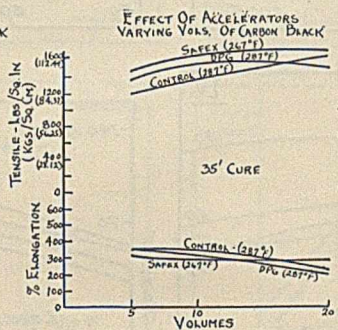


Figure 29

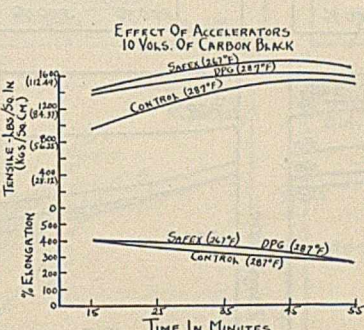


Figure 30

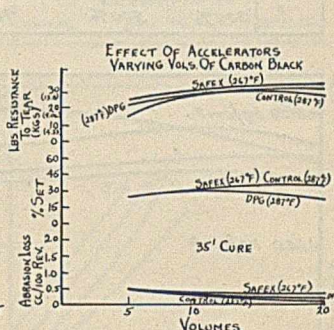


Figure 31

Safex were used as accelerators and the compounds were cured at 287° F. (142° C.) and 267° F. (131° C.), respectively. We therefore have the effect of reënforcing pigments with accelerators at both a high and moderately low temperature.

The physical properties of the reclaim containing varying volumes of Kadox with diphenylguanidine as the accelerator are the same as those obtained when no accelerator is used, with the exception of 20 volumes of Kadox which shows a slightly higher stress-strain curve. (Figures 24 and 25) Safex at 131° C. does not affect the rate of cure but increases the tensile strength (Figure 26) and resistance to abrasion. (Figure 27) Safex gives a very much higher stress-strain curve, accompanied by a lower elongation. It has no effect on the resistance to tear.

Diphenylguanidine and Safex increase the rate of cure and improve the tensile strength of a whole-tire reclaim containing varying volumes of carbon black. (Figures 29 and 30) The resistance to tear (Figure 31) is slightly improved,

whereas the accelerators give a higher stress-strain curve with 10 volumes of carbon black (Figure 28), but with 20 volumes Safex does not give any higher stress-strain curve than when no accelerator is used. This is probably due to the degree of cure obtained at the lower temperature.

Safex in a whole-tire reclaim containing varying volumes of clay or whiting gives improved tensile strength, resistance to tear and abrasion, and a higher modulus. The rate of cure is increased. Diphenylguanidine has very little effect other than increasing the rate of cure.

#### Effect of Low-Temperature Curing

It is logical to ask what benefits may be expected from low-temperature curing of a reclaim which in the course of its manufacture has been subjected to temperatures ranging from 350° to 385° F. (177° to 196° C.). The results of this study show that there is a distinct benefit to be derived by curing at lower temperatures.

## Effect of High vs. Low Sulfur in Vulcanizing Reclaim

R. E. Cartlidge and H. L. Snyder

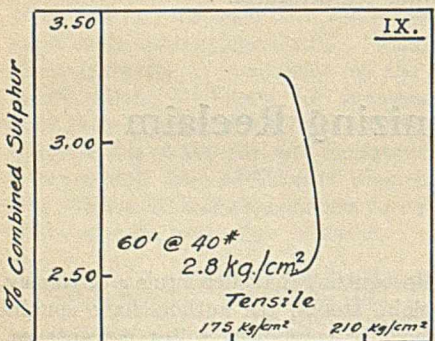
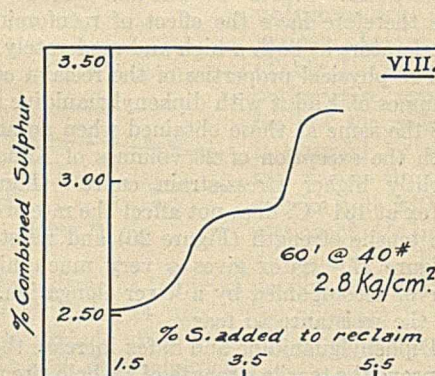
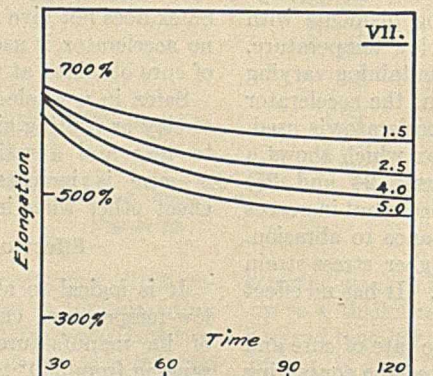
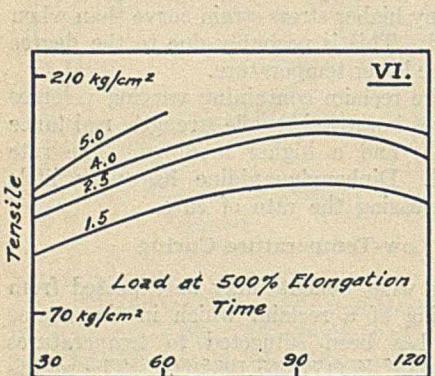
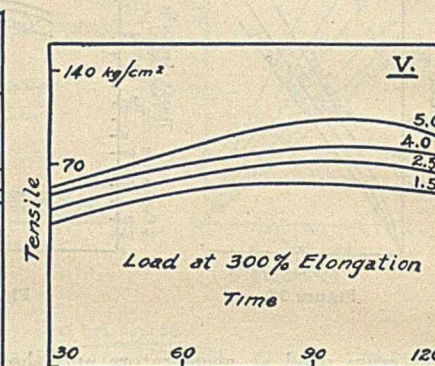
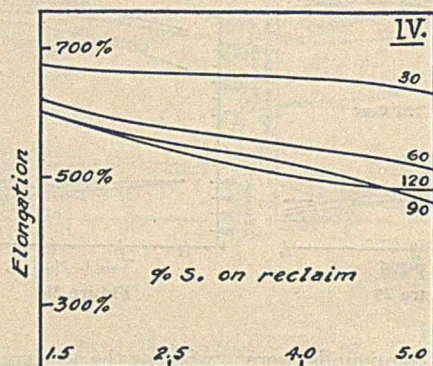
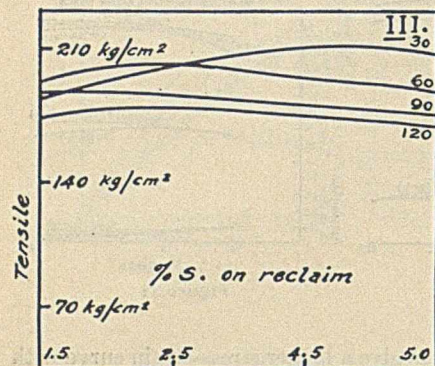
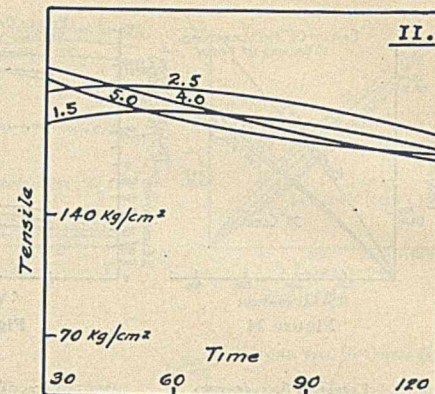
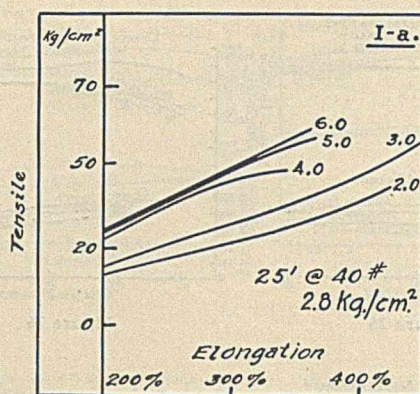
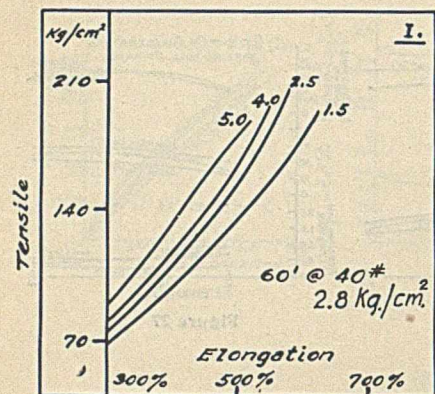
THE AKRON RUBBER RECLAIMING CO., BARBERTON, OHIO

MUCH progress has been made in determining what sulfur percentages will bring out the best quality of finished rubber, especially where organic accelerators are used, but this work has been done mostly with high-rubber stocks containing little or no reclaim. Now that reclaim has effectively entered into rubber compounding we find that there is no definite idea as to just what percentage of sulfur will give the optimum results in a compound containing a mixture of crude and reclaimed rubber. The general notion has been that approximately 4 per cent of sulfur on the total rubber content of the batch would be satisfactory in any stock with any kind of rubber-reclaim mixture, since such a value has worked well with crude-

rubber compounds. Recognizing that such a rule is obviously untrustworthy for reclaim stocks, the authors have sought a more accurate method for computing sulfur percentages. They submit this paper as merely preliminary to a subject which is vital to all compounders. The rubber content of the reclaim is considered to be the difference between the total unit weight of the reclaim and the sum of the parts by weight of acetone extract, ash, total sulfur, and carbon black.

#### Experiments with Straight Reclaim Stock

A sample of 45 kg. (100 pounds) of washed alkali tire reclaim was selected, and from it all the reclaim used in



the following tests was cut. By varying the sulfur percentages from 1.5 per cent to 6.0 per cent on the reclaim in straight reclaim-sulfur mixes one set of cures was obtained. These were made at intervals of 5 minutes. All cures were made at 142°

to the maximum percentage of sulfur present. This modulus also increases as the time of cure of any one sample increases. The ultimate tensiles of the 25-minute cure pass from a minimum at 2 per cent sulfur, or below, to an approximately constant maximum from 3 per cent up to and including the maximum amount of sulfur added.

Experiments with Compounded Stock

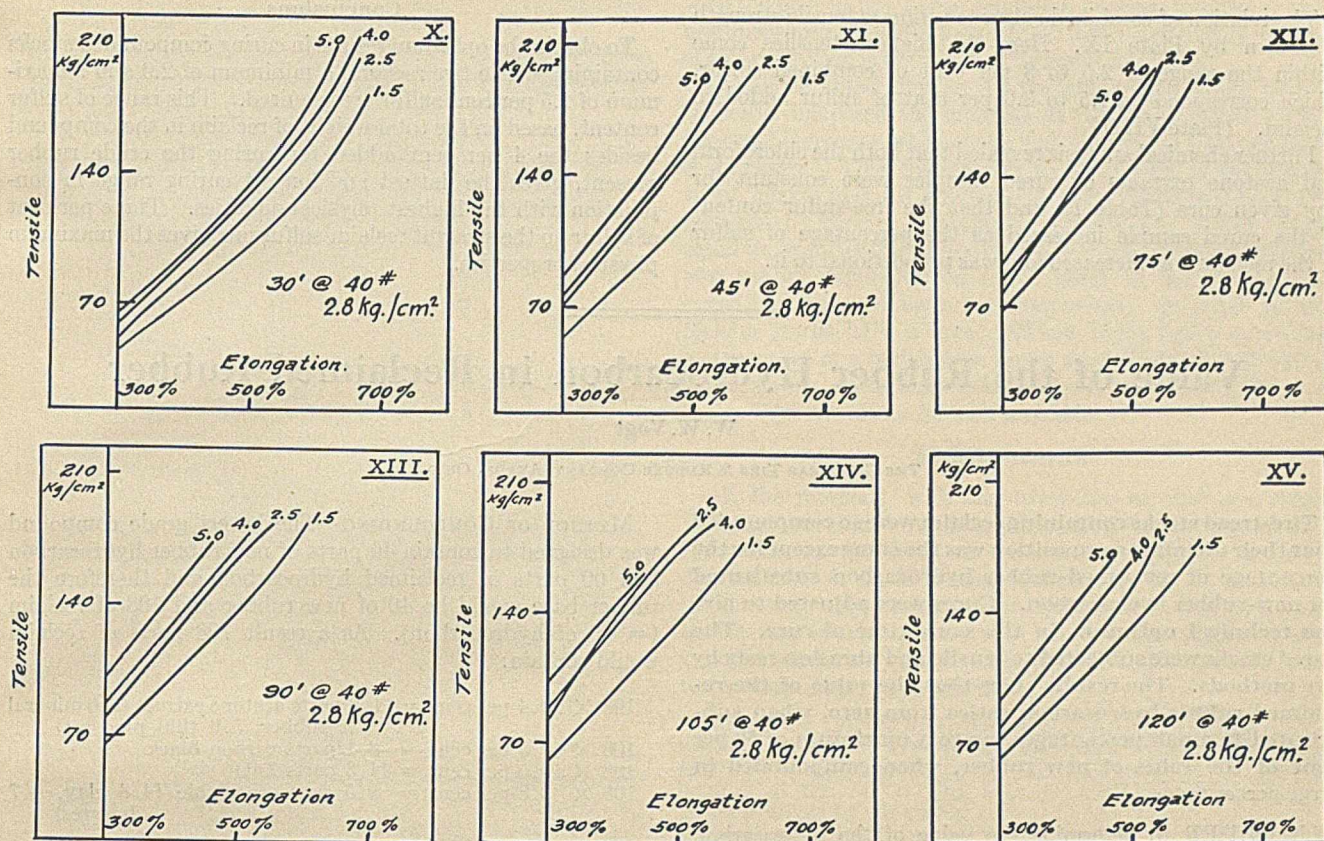
A typical tire-tread formula was used in making up the compounds for another set of cures to determine the effect of varying the sulfur in a compounded stock. Cures were made at 15-minute intervals.

FORMULA	
Parts	Parts
Rubber	35.0
Reclaim	35.0
Carbon black	17.0
Zinc oxide	5.0
Stearic acid	0.5
Mineral rubber	5.0
Sulfur	Variable
Accelerator	1.0

The sulfur percentages were varied from 1.5 per cent to 5 per cent on the reclaim. In all the compounds 4 per cent of sulfur was figured on the crude rubber present in addition to that added for vulcanizing the reclaim. Samples of the 60-minute cure for each compound were analyzed for

C. (287° F.) in the conventional type of horizontal press. Dumbbell test strips were cut from each slab and tested on a modified Olsen tensile machine, for loads at chosen elongations as well as breaking tensiles and elongations.

The results for the 25-minute cure indicate a surprising flatness after a minimum of 3.0 per cent of sulfur is added. Percentages less than that show undercure throughout. (Plate I-a) The only noticeable change in physical properties is in the stiffening of the modulus of rigidity progressively



free and combined sulfur and acetone and chloroform extracts. (Table I)

Table I—Analysis of Tread Stocks Cured 60 Minutes at 2.8 kg. per sq. cm. (40 lbs.) Pressure  
(Figures in per cent)

SULFUR IN RECLAIM	ACETONE EXTRACT	ACETONE EXTRACT (COR.)	TOTAL SULFUR	COMBINED SULFUR	FREE SULFUR	CHCl <sub>3</sub> EXTRACT
STOCK NO. 1						
1.5	4.25	3.89	2.83	2.47	0.36	0.88
2.0	4.39	3.98	2.94	2.53	0.41	0.68
2.5	4.57	4.13	3.06	2.62	0.44	0.81
3.0	4.23	3.78	3.30	2.85	0.45	0.82
3.5	4.46	4.00	3.35	2.89	0.46	0.73
4.0	4.88	4.36	3.44	2.90	0.54	0.72
4.5	4.86	4.33	4.01	3.46	0.55	0.83
5.0	5.08	4.35	4.20	3.47	0.73	0.79
STOCK NO. 2						
1.5	6.03	5.92	2.61	2.50	0.11	0.89
2.0	6.98	6.82	2.95	2.79	0.16	1.08
2.5	6.68	6.48	2.71	2.51	0.20	1.03
3.0	7.38	7.11	2.89	2.62	0.27	1.19
3.5	7.14	6.83	3.34	3.03	0.31	0.82
4.0	7.60	7.27	3.36	3.03	0.33	0.88
4.5	7.28	6.98	3.43	3.12	0.31	1.02
5.0	7.61	7.26	3.55	3.20	0.35	0.85

The effect of increasing curing time on the stress-strain curves is illustrated by Plates X, XI, XII, XIII, XIV, and XV in order mentioned.

As the time of cure increases the stress-strain curves show considerable shortening and a decrease in the angle formed with the Y axis, except in case of low-sulfur compounds. Therefore, with a sulfur content of 1.5 per cent, 2.5 per cent on the reclaim, better curing conditions were obtained for a longer curing time. Larger percentages of sulfur give proportionately greater changes in the position of the stress-strain curve of the various cures.

As the percentage of sulfur is increased to a maximum of 5 per cent on the reclaim, in addition to the 4 per cent added to the crude rubber, the ultimate tensile strength increases to a maximum, then decreases for all samples of each curing period. (Plate II)

In the 30-minute cure the tensile strength increases with increase in sulfur content up to 4 per cent, but with further increase in sulfur it decreases again. In the 60-minute cure 2.5 per cent of sulfur gives the maximum tensile strength and remains in this position throughout the remainder of the cures. The tensile strength curve in this plate passes through a maximum as the percentage of sulfur increases and then decreases on further increase in sulfur. It also shows that this maximum value, 2.5 per cent, holds for a longer duration of curing time than for any other sulfur percentages used. As the percentage of sulfur increases the rate of cure increases. (Plate III)

The greatest tensile strength is given by 4.5 to 5 per cent of sulfur at 30-minute cure; 2.0 to 2.5 per cent gives the best results at 60-minute cure, and equally as good tensiles at the 90- and 120-minute cures. This indicates also, as was demonstrated before, that 2.0 to 2.5 per cent of sulfur on the reclaim content of the compound gives the best average tensiles over any chosen curing range, up to the point of overcure. Increasing sulfur content causes a corresponding decrease in the ultimate elongation in each cure examined. (Plate VII) Also the ultimate elongation decreases as the time of cure increases. (Plate IV) The loads at 300 and 500 per cent elongation increase as the sulfur percentage increases. (Plates V and VI)

On overcuring there is a noticeable drop, indicating reversion. There is a proportional stiffening on modulus up to a maximum at the 90-minute cure, whence there is a slight falling off in load.

In Plate VIII combined sulfur is plotted against percentage of sulfur added to reclaim, independent of that taken as necessary for vulcanizing the crude rubber present. The combined sulfur is directly proportional to the per cent of sulfur added to the reclaim. This indicates that all the above statements concerning percentage of sulfur added are proportionately true of combined sulfur percentages.

The relation of combined sulfur to ultimate tensile strength is shown by Plate IX. Here the highest tensiles come within the range of 2.5 to 3 per cent of combined sulfur, which correspond to 1.5 to 3.0 per cent of sulfur added to reclaim. (Plate VIII)

Further chemical analysis revealed that both the chloroform and acetone extracts of cured samples were constant for any given cure (Table I), and that the free-sulfur content of the cured sample increased as the percentage of sulfur in the reclaim was increased and was proportional to it.

### Conclusions

To obtain the optimum results in curing compounded stocks containing whole tire reclaim, a minimum of 2.0 and a maximum of 2.5 per cent sulfur are required. This range of sulfur content, based on the total weight of reclaim in the compound besides the 4 per cent added for curing the crude rubber present, gives the flattest and longest curing range in conjunction with the highest physical qualities. Three per cent of sulfur on the straight reclaim-sulfur mix gives the maximum physical properties.

## Value of the Rubber Hydrocarbon in Reclaimed Rubber

W. W. Vogt

THE GOODYEAR TIRE & RUBBER COMPANY, AKRON, OHIO

Tire-tread stocks containing reclaim were so compounded that their ultimate composition was the same except for the percentage of reclaimed-rubber hydrocarbon substituted for new-rubber hydrocarbon. Cures were adjusted to give the technical optimum in the same time of cure. The cured stocks were subjected to tensile and abrasion tests by five methods. The results show that the value of the reclaimed-rubber hydrocarbon varies from zero, when substituted in small percentages, up to a maximum of 50 per cent of the value of new rubber, when compounded in large percentages.

**I**N ORDER to determine the value of the hydrocarbon present in reclaimed rubber compared with that in new rubber, it is necessary to compound the stocks in such manner that the percentage and kind of fillers, softeners, etc., are constant, the only variable being the percentage of the total rubber hydrocarbon which has been introduced in the form of reclaimed hydrocarbon. It is also necessary to adjust curing ratios in such fashion as to compensate for the accelerating or activating effects of the reclaim, so that all stocks reach technical best cure in the same length of curing time.

### Experimental

**COMPOSITION AND PROPERTIES OF RECLAIM**—The reclaim used was a typical high-grade, alkali-process, whole-tire reclaim having the following characteristics:

	Per cent
Acetone extract	10.4
Total sulfur	3.0
Free sulfur	0.08
Free carbon	7.5
Ash	19.3 (ZnO, 10.5, insoluble, 8.8)
Specific gravity	1.23

When cured in a formula consisting of 100 parts reclaim and 5 parts sulfur for 18 minutes at 2.8 kg. per sq. cm. (40 pounds) steam pressure (141.5° C.), it gave a tensile of 55 kg. per sq. cm. (800 lbs./sq. in.) and an elongation of 450 per cent.

The insoluble matter was assumed to be 50 per cent clay and 50 per cent barytes. The acetone extract was assumed to be 50 per cent mineral rubber and 50 per cent thin pine tar. The hydrocarbon content of the reclaim was figured at 55 per cent.

*Note*—These assumptions are in line with general experience with this type of reclaim. Furthermore, the exact ratio of clay to barytes makes very little difference in the ultimate physical properties of the compounds inasmuch as neither contributes any marked qualities to the final rubber compounds. The same may be said of the acetone extract. Outside of effects on the rate of cure, which have been compensated for in another manner, the type of softener assumed is unimportant. The rather high percentage of pine tar assumed was based on the knowledge that some of this material was used in the reclaiming process.

**METHOD OF COMPOUNDING**—The lowest grade compound was designed to contain 40 parts of new rubber hydrocarbon and 60 parts of reclaimed hydrocarbon and therefore the rubber base would be 40 of new rubber and 108 of reclaim (= 60 of hydrocarbon). As a result 108 parts of reclaim would contain:

$$\begin{aligned}
 108 \times 10.4 \text{ per cent} &= 11.2 \text{ parts acetone extract (5.6 mineral rubber, 5.6 thin pine tar)} \\
 108 \times 7.5 \text{ per cent} &= 8.1 \text{ parts carbon black} \\
 108 \times 10.5 \text{ per cent} &= 11.3 \text{ parts ZnO} \\
 108 \times 8.8 \text{ per cent} &= 9.5 \text{ parts insoluble (4.8 clay, 4.7 barytes)}
 \end{aligned}$$

Hence, these quantities of the various fillers and softeners will be unavoidably introduced in the lowest grade compound. The base compound containing all new rubber must then be made to contain these additions, in order to secure constancy of composition over the series.

It was known that the accelerating or activating effect of the reclaim could be duplicated by adding a small amount of litharge to the new-rubber base stock, so 0.5 part of the rubber was added to the base stock and this amount decreased in successive formulas as reclaim was added. This expedient gives a practically uniform rate of cure throughout the series. The complete formulas are given in Table I.

Table I—Stock Formulas

Stock	1	2	3	4	5	6	7
% Reclaim hydrocarbon	0	5	10	20	30	45	60
Pale crepe	100	95.0	90.0	80.0	70.0	55.0	40.0
Reclaim	0	9.0	18.0	36.0	54.0	81.0	108.0
ZnO	16.5	15.5	14.6	12.7	10.8	8.0	5.0
Gas black	43.0	42.3	41.6	40.3	39.0	36.9	35.0
Clay	4.8	4.6	4.4	3.2	2.4	1.2	0.0
Barytes	4.7	4.5	4.3	3.1	2.3	1.1	0.0
Mineral rubber	5.6	5.1	4.6	3.7	2.8	1.4	0.0
Pine tar	5.6	5.1	4.6	3.7	2.8	1.4	0.0
Litharge	0.5	0.45	0.4	0.32	0.23	0.1	0.0
Stearic acid	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Sulfur	3.5	3.5	3.5	3.5	3.5	3.5	3.5
Captax	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Total	189.2	190.05	191.0	191.52	192.83	194.6	196.5

These stocks were milled in about 4-kg. batches on a 50-cm. (20-inch) laboratory mill. The mineral rubber was added to the new rubber. The gas black and the accelerator were added in the form of a master batch. The new rubber containing the mineral rubber, the gas black master batch, and the separately broken-down reclaim were blended together and the rest of the ingredients added to the batch. Further compounds were made up in the following manner: New batches of stocks 1, 6, and 7 were milled and with the excess stock of the remaining batches were combined in such proportions by weight as to duplicate the chemical composition of stocks 1 to 7 (Table II). By so doing it was thought that

some light might be cast on the question as to whether the law of mixtures was obeyed.

The results of this series confirmed those of the first series so exactly that it was concluded that the law of mixtures holds.

Table II—Composition of Mixed Stocks

Stock	21	22	23	26	24	28	25	29	30
% Reclaim hydrocarbon	0	5	10	10	20	20	30	45	60
Stock	1	1	1	2	2		1		
1									
2									
3		1					1		
4			1						
5				1			1		
6								1	
7									1

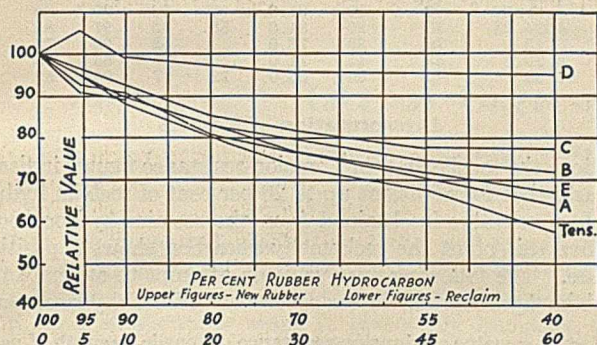


Figure 1

**TESTING PROCEDURE**—Standard procedures for physical testing were followed throughout, with care to give all stocks similar treatment. A range of cure from 30 to 90 minutes at 126° C. (258° F.) was obtained and the tensiles were practically identical over this range for all stocks. Hence the results on tensile are quite independent of cure. The abrasion results were obtained on the 60-minute cure for all stocks. This was judged to be the technical optimum.

All the data given are the average results secured from at least two, and in some cases three, batches of each stock, involving separate sets of cures. The tensile data are the average of all cures in the flat part of the curing curve, so that each point in Figure 1 represents at least two batches of four cures of three strips (two highest), or twenty-four separate tensile determinations. The abrasion data represent at least two batches of one cure of two test pieces on each type of machine. Since the conditions were so varied on the different types of abrasion machines, the data are presented in a comparative manner using stock 1 as a standard.

#### Tensile Strength and Other Physical Tests

The values for tensile strength for all the stocks are given in Table III.

Table III—Tensile Strength of Various Stocks

Per cent reclaim hydrocarbon	0	5	10	20	30	45	60
Per cent new-rubber hydrocarbon	100	95	90	80	70	55	40
Stocks	Kilograms per square centimeter						
	1	2	3	4	5	6	7
	21	22	23	24	25	29	30
Tensile	290	275	255	230	210	195	170
	280	270	255	230	220	200	175
			255	235			
Average tensile	285	272	255	232	215	197	172
Tensile as per cent of stock 1	100	95.5	89.5	81.5	75.5	69	60

The results are shown graphically in Figure 1, as is also the relative abrasion resistance by methods A to E as shown in Table V. Further data on the stress-strain properties of the best cure (60 minutes at 126° C.) of the stocks are given in Table IV, together with other data as to hardness, etc. The mechanical efficiency was obtained on small blocks of rubber by means of a pendulum rebound machine. At the same

time the penetration of the pendulum hammer into the rubber was measured to 0.001 inch (0.025 mm.) and the reciprocal of this deflection is termed the "dynamic hardness."

It will be noted that as the percentage of reclaim hydrocarbon is increased the modulus at the low elongation (200 per cent) increases, while at the high elongation (500 per cent) it decreases. This corresponds to a rotation of the stress-strain curves about a point of constant modulus (about 400 per cent). Stocks containing reclaim are stiffer than, equal to, or softer than the equivalent stock compounded from new rubber depending on which point of the stress-strain curve is used as a basis for comparison. In other words, reclaim stocks have a lower stiffness index figure according to Dinsmore or a higher type figure according to Schidrowitz. Both writers agree that either a lower stiffness index or a higher type means an inferior product.

#### Abrasion Results

All the methods, with the exception of that one using Williams' machine<sup>1</sup> (Grasselli abrader), made use of test specimens in the form of annular rings of the following dimensions: o. d., 87.5 mm. (3.5 inches); i. d., 50.0 mm. (2.0 inches); thickness, 17.5 mm. (0.68 inch). The periphery of the ring makes contact with the abrasive surface under suitable conditions of slip. The abrasive surface in all cases was a 36-grain alundum wheel.

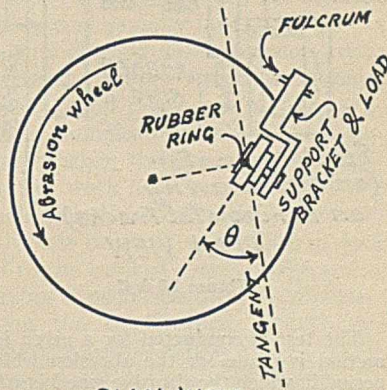
**METHOD A (Figure 2A)**—The ring is set perpendicular to the abrasive surface and at an angle with respect to the tangent of the abrasive wheel which passes through the center of the area of contact of the rubber ring and the abrasive. The abrasive wheel is driven by the motor.

#### Conditions:

Angle ( $\theta$ )	16 degrees
Load applied on rubber ring	14.5 kg. (32 lbs.)
R. p. m. of abrasive wheel	80
Surface speed of abrasive wheel at center of area of contact with rubber ring	137 meters (450 feet) per minute
R. p. m. of rubber ring	About 500

#### METHOD B (Figure 2B)

—An abrasive wheel is mounted coaxially with a heavy flywheel. The rubber ring is mounted on the shaft of a constant-speed motor, which is in turn mounted on a freely moving carriage. A weight is used to press the rubber ring against the periphery of the abrasive wheel. It will be appreciated that the flywheel system has a constant moment of inertia and that if the rotating rubber ring is placed in contact with the stationary abrasive wheel slippage, and consequently abrasion, will take place until the abrasive wheel is running at the same surface speed as the rubber ring. Furthermore, a definite amount of energy must be supplied to the flywheel system to bring it to this condition. As a result a certain amount of rubber will be abraded while a definite quantity of energy has been transmitted through the rubber ring to the flywheel system. The loss per cycle is taken as the unit of measurement. The principle of this machine was suggested by A. M. Hamblet.



PLAN VIEW

Figure 2A

#### Conditions:

R. p. m. of rubber ring	1780
R. p. m. of abrasive wheel	0 to 515
Surface speed of rubber ring	450 meters (1625 feet) per min.
Surface speed of abrasive wheel	0 to 495 meters (0 to 1625 feet) per minute
Load applied	2.27 kg. (5 lbs.)

**METHOD C (Figure 2C)**—The same set-up is used as in method B. A tachometer is mounted on the flywheel shaft and when

<sup>1</sup> Ind. Eng. Chem., 19, 674 (1927).

Table IV—Physical Properties of Stocks

STOCK	RECLAIM HYDROCARBON %	MODULUS				AV. TENSILE Kg. per sq. cm.	ELONGATION %	SHORE HARDNESS	DYNAMIC HARDNESS	MECHANICAL EFFICIENCY %
		200%	300%	400%	500%					
1	0	47	85	135	198	285	625	70	4.38	63.1
2	5	51	88	140	195	272	600	71	4.62	64.2
3	10	48	85	132	190	255	595	72	4.80	60.0
4	20	52	86	134	186	232	580	71	5.02	57.0
5	30	52	88	132	182	215	560	71	5.02	56.5
6	45	57	93	134	178	197	540	72	5.02	58.0
7	60	57	93	131	172	172	500	71	4.95	59.0

the system is running at maximum speed a strap brake is applied to the flywheel to cut down its speed any given amount. Since the rubber ring is maintained at constant speed, a certain differential slip is set up and abrasion ensues. The test is continued for a given length of time, and from the value of loss so obtained is subtracted the loss due to one cycle (of method B).

The general conditions were the same as in method B. The slip was calculated as the reduction in r. p. m. of the abrasive wheel divided by the maximum r. p. m. of the abrasive wheel times 100. The value used in the present experiments was 30 per cent, corresponding to a surface slip of about 150 meters (500 feet) per minute.

METHOD D (Figure 2D)—The rotating rubber ring is pressed against the abrasive wheel, but the plane of the rubber ring makes an angle ( $\theta$ ) with the plane of the abrasive wheel. This sets up a slippage with consequent abrasion.

Conditions:	
Angle ( $\theta$ )	20 degrees
Load on rubber ring	2.27 kg. (5 lbs.)
R. p. m. of rubber ring	1780
Surface speed of rubber ring	495 meters (1625 feet) per minute
Surface speed of abrasive wheel	$1625 \times \cos \theta = 465$ meters (1530 feet) per minute
Maximum r. p. m. of abrasive wheel	485
Slip	$1625 \times \sin \theta = 170$ meters (555 feet) per minute

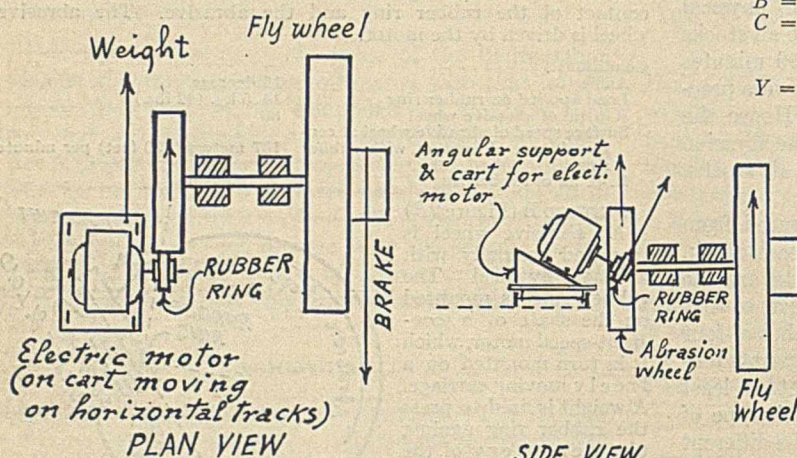


Figure 2B &amp; C

Figure 2D

The test is conducted for a given length of time and no correction is made for the abrasion which takes place during the period in which the abrasive wheel is attaining its maximum speed.

METHOD E—The Grasselli abrader (Williams' machine) is used according to the standard conditions recommended by Williams:<sup>1</sup> load, 3.64 kg. (8 lbs.); time, 20 minutes.

The results are figured on the basis of cubic centimeters per horsepower-hour. All these methods gave duplicable results, and seldom was the maximum variation as much as 5 per cent. The mean variation was 2 to 3 per cent.

A summary of the averages of all stocks 1 to 7 and 21 to 30 by the various methods is given in Table V, wherein the values given are for abrasion resistance with the all new-rubber stock 1 assigned an arbitrary value of 100. Values less than 100 indicate inferior wearing stocks. Method D gives results which show that all stocks are virtually the same. Since the only property which is approximately constant for all stocks is their hardness, it might be inferred that this method measures hardness almost exclusively. The other methods, particularly A and E, agree very well.

Table V—Abrasion Resistances (Figure 1)

STOCK	NEW-RUBBER HYDRO-CARBON %	RE-CLAIM HYDRO-CARBON %	METHOD				
			A	B	C	D	E
1, 21	100	0	100	100	100	100	100
2, 22	95	5	93	95	96	106	91
3, 23, 26	90	10	91.0	90	92	99	89
4, 24, 28	80	20	81.0	83	85	97	83
5, 25	70	30	77.0	..	82	96	77
6, 29	55	45	71.0	75	77	95	72
7, 30	40	60	65.0	72	77	95	67

### Interpretation of Results

Both the tensile and the abrasion-resistance figures indicate clearly that for additions up to 20 per cent of reclaim hydrocarbon no value is obtained from the reclaim hydrocarbon. Above this point the reclaim hydrocarbon shows a positive value. The following analysis is an attempt to evaluate the reclaim hydrocarbon in terms of new-rubber hydrocarbon:

Let  $A$  = value of abrasion resistance or tensile strength of new-rubber hydrocarbon, and let it be assigned a value of 100 units

$B$  = value of reclaim hydrocarbon in the same units

$C$  = experimentally determined values for abrasion resistance or tensile strength (based on new-rubber stock = 100) of various stocks

$Y$  = amount of new-rubber hydrocarbon as a decimal fraction and  $1.00 - Y$  = amount of reclaim hydrocarbon as a decimal fraction

Then  $Ay + B(1.00 - y) = C$  on the assumption that the qualities of the two types of hydrocarbons are additive.

$$\text{Solving for } B = \frac{C - Ay}{1.00 - y}$$

The  $B$  value is the intercept on the vertical axis in Figure 1 at the 100 per cent reclaim point of a line drawn from the 100-unit point on the vertical axis through any experimental point on the various curves. Taking the values of  $C$  for tensile strength from Table III and the values for abrasion resistance from Table V and solving for  $B$  we get the figures given in Table VI.

These values apply to the particular methods of testing used and to the particular stocks employed, and since the value changes with the amount of reclaim hydrocarbon substituted for new-rubber hydrocarbon, it is not capable of general application. The method of evaluation might, however, be profitably extended to various types of compounds and to various methods of testing.

Table VI—Values of Reclaim Hydrocarbon

NEW-RUBBER HYDRO-CARBON %	RE-CLAIM HYDRO-CARBON %	FROM TENSILE STRENGTH	FROM ABRASION RESISTANCE BY METHODS				
			A	B	C	D	E
100	0	..	..	..	..	220 (?)	..
95	5	0	Neg.	0	20	90	Neg.
90	10	Neg.	1	0	20	90	Neg.
80	20	0	5	15	25	85	15
70	30	10	23	..	40	86	23
55	45	27	35	45	49	89	38
40	60	30	42	33	62	92	37

These results might be construed to mean that reclaim is worthless when used in small amounts in high-grade tread compounds. This is by no means a fact. They do mean, however, that a method of compounding which substitutes reclaimed hydrocarbon for new-rubber hydrocarbon without other changes and adjustments in the formula may give adverse results.



Holt and Wormeley<sup>2</sup> published results of road tests and laboratory abrasion tests on tire treads containing reclaim. The writer has recalculated the composition of the compounds listed by them (page 580) on the same basis as used in the present paper and on the assumption that the reclaim used had the same analysis as that used here. Table VII gives some comparisons.

In spite of the fact that the substitution of new-rubber hydrocarbon by reclaimed-rubber hydrocarbon is accompanied by an increase in the percentage of carbon black (the main reinforcing pigment), the wear resistance drops off faster than the percentage of new-rubber hydrocarbon,

<sup>2</sup> *Bur. Standards, Tech. Paper 294.*

thus giving negative values for the reclaim hydrocarbon. These results confirm in the main the conclusions of the present paper.

Table VII—Comparison of Laboratory and Road Tests

Stock	1A	1B	1C	1D
Per cent new-rubber hydrocarbon	100	90.4	82.7	76
Per cent reclaim hydrocarbon	0	9.6	17.3	24
Parts carbon black per 100 total hydrocarbon	26.2	28.2	30.0	31.2
Parts ZnO per 100 total hydrocarbon	20.5	21.4	18.0	15.5
Road-wear index	100	85	80	73
B value		Neg.	Neg.	Neg.

#### Acknowledgment

The writer wishes to express his appreciation to R. P. Dinsmore for valuable suggestions and criticism.

## Rate of Cure of Reclaimed Rubber

Norman A. Shepard, Henry F. Palmer, and George W. Miller

THE FIRESTONE TIRE AND RUBBER COMPANY, AKRON, OHIO

Data are presented emphasizing the well-known fact that reclaimed rubber vulcanizes at a much more rapid rate than new rubber, and that, even in small concentration, in a new rubber stock it materially increases the rate of cure. Possible reasons for this are discussed and experimental evidence given to show the influence of the residual alkali in the reclaim, and the effect of the heat treatment in itself. Neither of these explains the rapid rate. The need for, and methods of, compensating for this rapid rate of cure in compounding with reclaimed rubber are discussed, with especial emphasis on the influence of the rapid rate of cure on the aging characteristics of a stock.

IN SPITE of the enormous importance of reclaimed rubber the literature on this material, aside from patents, is extremely meager. Especially is this true with reference to the properties and methods of using reclaimed rubber. Such properties as tensile, elongation, resistance to tear, and resistance to wear, both of reclaimed rubber itself and of products in which reclaimed rubber has been combined with new rubber, have been discussed at considerable length in recent publications<sup>1,2,3</sup> and also as far back as 1902,<sup>4</sup> but the rate of cure of reclaimed rubber, which is of paramount importance in connection with the proper re-use of reclaim has received little or no mention. In the controversy between Ditmar<sup>5</sup> and Alexander<sup>6</sup> concerning the chemical identity of regenerated rubber and vulcanized rubber, the former asks, "How else does Alexander explain the fact that reclaimed rubber vulcanizes much more quickly than raw rubber?" and Alexander replies, "I do not know that this fact has yet been established by exact experiments and I doubt if it can be accepted as generally true." And still today, as far as the writers are aware, no proof of this rapid rate of cure appears in the literature. Bierer and Davis,<sup>2</sup> Winkelmann,<sup>3</sup> Weber,<sup>7</sup> and Palmer<sup>8</sup> all refer to the physical properties of very short cures of reclaim-sulfur mixtures, without commenting on the short length of these cures as compared with those necessary when new rubber is used

with a similar concentration of sulfur. Winkelmann<sup>3</sup> shows that the rate of cure of reclaimed rubber is influenced but slightly by organic accelerators, experimentally confirming an anonymous statement to that effect made several years earlier.<sup>9</sup> Alexander<sup>6</sup> and Pickles<sup>10</sup> advanced possible causes for the increased rate of cure in the presence of reclaim, but gave no experimental data. Apparently the "two of the largest tire manufacturers in the country," which furnished Holt and Wormeley<sup>1</sup> with the compounds for their work on the wear resistance of tire treads containing reclaimed rubber, were unaware of the rapid rate of cure of reclaimed rubber, or else completely ignored it, for even though introducing into their formulas as much as 25 per cent of reclaim, the sulfur content, already high (4.9 per cent), was not reduced and the accelerator concentration actually increased.

Inasmuch as the literature afforded no experimental data on the rate of cure of reclaimed rubber versus new rubber, the writers have undertaken to fill this gap. In Figures 1, 2, and 3 are plotted data on samples of whole-tire, carcass, solid-tire, and tube reclaims, when tested against new rubber (smoked sheets). In this work 5 per cent of sulfur was added to the whole-tire reclaim and the corresponding amount based on the respective rubber contents was added to each of the other reclaims and to the smoked sheets. The actual proportion of sulfur to rubber in each case was 8.3 per cent.

In the writers' opinion the relationship between the rates of cure in these mixtures is best seen in Figure 1. With increase in curing time these so-called "modulus" curves rise to a peak and then fall off. In other words, the stress required to produce a given elongation increases with cure up to a maximum, beyond which a decrease in stress occurs—i. e., a lesser load is required to produce the same elongation. Without entering into the controversy as to the best method of selecting the "optimum" cure,<sup>11</sup> the writers have arbitrarily chosen to use the peak in the curve in which time of cure is plotted against stress at a given elongation as the point of reference in comparing rates of cure. This has been selected in preference to the peak in the tensile-time, or tensile product *vs.* time, curve, inasmuch as the points on these latter curves are more difficult to determine accurately, owing to the fortuitous and erratic nature of the breaking point.

Judging from the peak in the modulus curves of Figure 1,

<sup>1</sup> Holt and Wormeley, *Bur. Standards, Tech. Paper 294* (1925).

<sup>2</sup> Bierer and Davis, *Ind. Eng. Chem.*, **18**, 348 (1926).

<sup>3</sup> Winkelmann, *Ibid.*, **18**, 1163 (1926).

<sup>4</sup> Weber, *India Rubber J.*, **23**, 511, 561 (1902).

<sup>5</sup> *Gummi-Ztg.*, **21**, 694, 730 (1907).

<sup>6</sup> *Ibid.*, **21**, 708 (1907).

<sup>7</sup> "Chemistry of Rubber Manufacture," Charles Griffin and Co., Ltd. (1926).

<sup>8</sup> *Ind. Eng. Chem.*, **19**, 1030 (1927).

<sup>9</sup> *Caoutchouc & gutta-percha*, **15**, 9512 (1918).

<sup>10</sup> *India Rubber J.*, **60**, 957 (1920).

<sup>11</sup> Wiegand, *Ind. Eng. Chem.*, **18**, 1157 (1926).

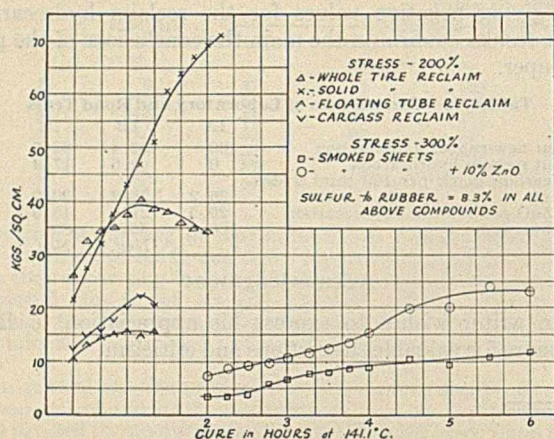


Figure 1—Stress at Given Elongation vs. Time of Cure of Reclaim and New Rubber

all the samples of reclaim are very much faster in curing rate than smoked sheets, whether the latter are cured in the presence or absence of zinc oxide. The floating-tube reclaim (alkalinity as NaOH 0.12 per cent) reaches its maximum modulus in 1 hour, the whole-tire reclaim (alkalinity 0.10 per cent) in 1 hour and 10 minutes, and the carcass reclaim (alkalinity 0.10 per cent) also in 1 hour and 10 minutes. The solid-tire reclaim (alkalinity 0.016 per cent), which was the only one of the four reclaims made without the use of alkali, is appreciably slower in curing rate as judged by the peak in the curve. The 200 per cent modulus curve is still rising at the end of 2 hours and 10 minutes; beyond that cure rupture occurred below an elongation of 200 per cent, but the 100 per cent elongation figures (not shown in the graph) on longer cures show that the peak was reached in 2 hours and 10 minutes.

Table I—Stress at 100% Elongation  
(Kg. per sq. cm.)

130 min.	150 min.	170 min.
38	35.5	37.5

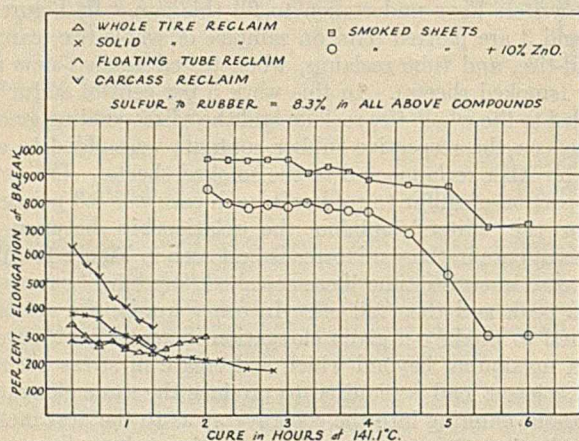


Figure 2—Elongation vs. Time of Cure Curves of Reclaim and New Rubber

In the case of the new rubber in the absence of zinc oxide no definite peak is reached with smoked sheets in 6 hours; in the presence of 10 per cent of zinc oxide the peak occurs apparently at 5 hours and 30 minutes. In other words, the slowest curing reclaim—i. e., the solid-tire reclaim—reached its optimum cure in less than half the time required by the smoked sheets containing 10 per cent of zinc oxide, while the fastest curing sample of reclaim—the tube reclaim—cured to optimum modulus in almost one-sixth the time.

This remarkably fast rate of cure of reclaimed rubber persists to a surprising extent when reclaim is introduced as a compounding ingredient. This is very clearly shown in Figure 4, where the modulus curve for a practically pure gum mixture (I) accelerated with di-*o*-tolylguanidine is shown compared with a similar stock containing 15 per cent of carcass reclaim of 90 per cent rubber content (II). The pigments present in the reclaimed rubber were compensated for, so that there was no increase in pigmentation. In this replacement guayule was treated as all rubber, and subsequent tests show that this did not influence the result.

	I	II
Carcass reclaim	...	16.3
Smoked sheets	96.5	83.6
Guayule	3.5	...
Sulfur	3	3
Zinc oxide	2.75	1.2
Mineral rubber	3.25	3.25
Di- <i>o</i> -tolylguanidine	0.5	0.5
	109.50	107.85

In spite of the quite high organic accelerator content in both cases, the mixture containing the reclaim shows a much more rapid rate of cure, reaching its optimum in 45 minutes at 143.4° C. as compared with 60 minutes for the mixture containing no reclaim. Perhaps even more striking is Figure 5, in which a practically pure gum mixture (III)

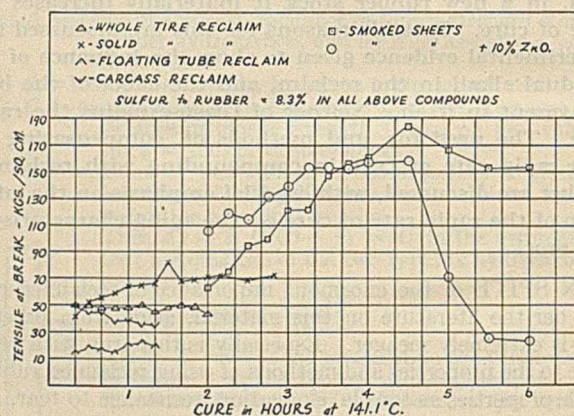


Figure 3—Stress at Break vs. Time of Cure Curves of Reclaim and New Rubber

accelerated with aldehyde ammonia is shown with 5 (IV), 10 (V), and 15 (VI) per cent of carcass reclaim. As is seen from the formulas, in introducing the reclaim for rubber the rubber in the reclaim (calculated as 87 per cent rubber) replaces smoked sheets, and the pigment in the reclaim is taken out of the zinc oxide.

	III	IV	V	VI
Carcass reclaim	...	5	10	15
Smoked sheets	69.5	65	60.75	56.5
No. 3 amber crepe	10	10	10	10
Caucho ball	7	7	7	7
Guayule	4	4	4	4
Sulfur	3	3	3	3
Zinc oxide	2.5	2	1.25	0.5
Aldehyde ammonia	1	1	1	1
Liquid asphalt	3	3	3	3
	100.0	100.0	100.0	100.0

While the mixture containing no reclaim had apparently not reached its optimum within 90 minutes at 132.2° C., that containing 5 per cent of reclaim reached its optimum in 60 to 75 minutes, that containing 10 per cent in 45 to 60 minutes, and that containing 15 per cent in 30 minutes.

In highly pigmented compounds, such as treads, the influence of reclaim on the rate of cure is somewhat masked by the high pigmentation, and therefore larger amounts of reclaim are necessary in illustrating its effect on rate of cure. In Figure 6 a highly compounded tread is shown containing

5 per cent (VII) and 35 per cent (VIII) of whole-tire reclaim. While the 5 per cent reclaim stock reached its optimum cure in 90 to 105 minutes at 143.4° C., the corresponding mixture containing 35 per cent of reclaim reached its optimum in 60 minutes.

	VII	VIII
Smoked sheets	60	21.5
Amber crepe	30	30
Rolled brown crepe	10	10
Whole-tire reclaim	9	62
Zinc oxide	10.75	2
Sulfur	3	2.75
Gas black	48	41.5
Pine tar	7	5.25
Di-o-tolylguanidine	1	0.95
	178.75	175.95

### Possible Causes of Rapid Rate of Cure

As far as the writers are aware, the cause or causes for this rapid rate of cure of reclaimed rubber have never been investigated. In the case of alkali

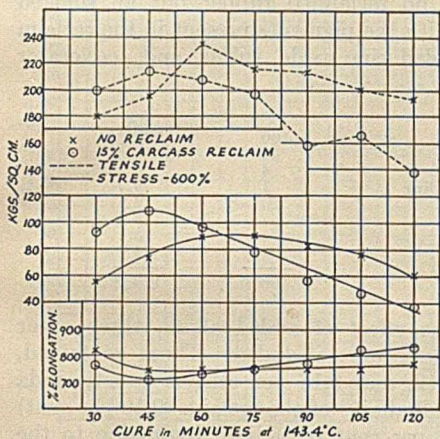


Figure 4—Effect of Carcass Reclaim on Rate of Cure of Friction Compound I

reclaims it is logical to assume that residual alkali plays a part, for it is well known that sodium and potassium hydroxides and carbonates are active accelerators of vulcanization, as has been shown by Martin,<sup>12</sup> Eaton,<sup>13</sup> van Heurn,<sup>14</sup> and others. This is the opinion of Pickles,<sup>10</sup> who writes in 1920: "Some firms are just learning now that reclaim made under the alkali process possesses considerable accelerating power, but this is probably because a certain amount of caustic potash is still left in the rubber even after washing and drying." Residual accelerator, other than caustic, might also be responsible for the rapid rate of cure. This is also the opinion of Alexander,<sup>6</sup> who attributes the rapid rate of cure of certain reclaimed rubbers to the presence of litharge in the scrap from which it was made. These, however, are only two of the possible causes for the rapid rate of cure of reclaimed rubber.

During the process of reclaiming, rubber is subjected not only to very high temperatures, upward to 191.9° C. (175 lbs. steam pressure), but also to excessive milling or mechanical working. Following the high temperature "cook" in an autoclave, the rubber, after drying, is mechanically worked on mills until the scrap has knit together. It is then transferred to refiners, which consist of two heavy rolls set very close together, where the reclaim is milled out into a thin sheet to remove the coarse, incompletely devulcanized pieces of rubber known as "tailings." The result of this working, both at the massing mill and the refiner, is a marked increase in plasticity. Both heat and mechanical working have been shown to increase the reactivity of the rubber hydrocarbon. Axelrod<sup>15</sup> found that heating Para rubber for even so short a period as 30 minutes at 120° C. caused it to take up sulfur at a faster rate, as shown by the vulcanization coefficient after a given time of cure. The exact conditions under which the rubber was heated are not clear.

The same author also compared the rate of cure of washed Para rubber before and after working on a mixing mill. He again found that the sulfur added more rapidly to the rubber which had been milled. Harries<sup>16</sup> has stated that rubber which has been heated in xylene, or which has been thoroughly masticated, shows a marked increase in reactivity toward permanganate, "apparently having become depolymerized" by these treatments. Staudinger and Fritsch<sup>17</sup> found it necessary in order to hydrogenate rubber to use both high temperature and high pressure, while Harries<sup>18</sup> was successful in hydrogenating rubber at ordinary temperatures only when he first subjected the rubber to strong plasticization. Fisher and Gray<sup>19</sup> have shown that neither heating rubber nor masticating it results in a higher degree of unsaturation, as judged by its ability to take up iodine. In fact, when these investigators heated pale crepe in a steel tube for 7 hours at 285–300° C., temperatures in excess of those ordinarily used in the devulcanization of rubber, they found a decrease in the unsaturation of the material. Their results strongly indicate that heat and mastication do not depolymerize rubber in a chemical sense, but rather produce a physical disaggregation, which would increase the reactivity of the rubber due to decrease in the size of the particle, and therefore increase in the surface. However this may be, analogy certainly would indicate that the increased rate of cure of reclaimed rubber may be caused by the action of heat and mastication.

Again, the increased rate of cure might be ascribed to the "head start" of the reclaim with respect to chemical state of cure. Whole-tire reclaim ordinarily contains approximately 3 per cent of combined sulfur. Allowing for the pigment, softener, and other non-rubber substances, this combined-sulfur content amounts to approximately 5 per cent of the rubber. While this figure does not represent the

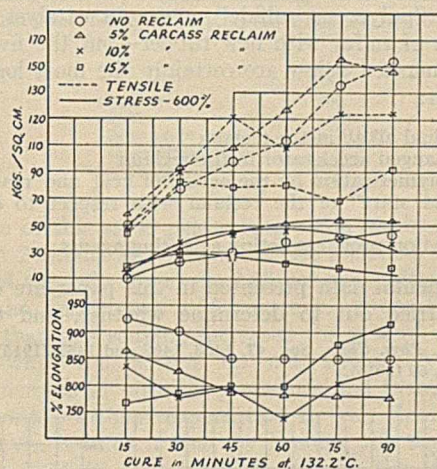


Figure 5—Effect of Carcass Reclaim on Rate of Cure of Friction Compound III

actual amount of sulfur combined with the rubber, as some of the combined sulfur is undoubtedly combined with pigment, resins, etc., it does indicate very definitely that the sulfur coefficient is very high. It is conceivable, therefore, that reclaimed rubber with such a high coefficient of vulcanization might require the addition of less sulfur to bring it back to the vulcanized elastic state, in which case it should not take so long to cure it.

A further viewpoint is that oxygen may play a part. The scrap from which reclaimed rubber is made contains the

<sup>12</sup> "Rubber Industry," p. 205 (1914); *J. Soc. Chem. Ind.*, **34**, 725 (1915).

<sup>13</sup> *Agr. Bull. Federated Malay States*, **4**, 162 (1916).

<sup>14</sup> *Neth. Gov. Inst. Bull.*, Pt. VI, 201 (1916).

<sup>15</sup> *Gummi-Ztg.*, **24**, 352 (1909).

<sup>16</sup> *Ann.*, **406**, 198 (1914).

<sup>17</sup> *Helv. Chim. Acta*, **5**, 785 (1912).

<sup>18</sup> *Ber.*, **56**, 1050 (1923).

<sup>19</sup> *Ind. Eng. Chem.*, **18**, 414 (1926).

rubber in a partially perished and oxidized condition. During the devulcanization process some air is ordinarily present and it is probable that a certain amount of oxygen combines with the rubber during the devulcanization process at high temperature. That such oxidation products could influence the rate of cure is not inconceivable, for it is well known that rubber undergoes a sort of "vulcanization" under the influence of oxygen. This has been clearly shown by the work of Ostromuiskii,<sup>20</sup> who has effected such a

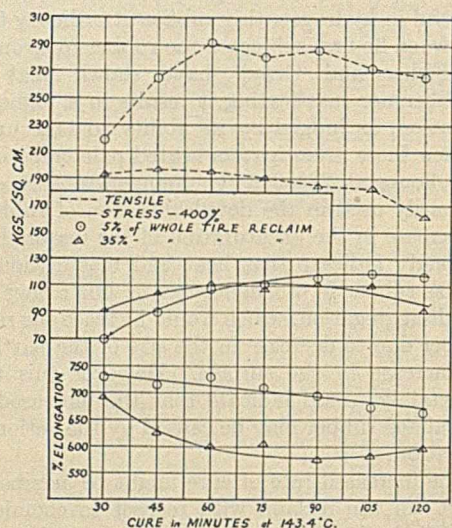


Figure 6—Effect of Whole-Tire Reclaim on Rate of Cure in Tread Compounds VII and VIII

change through the use of polynitro compounds or benzoyl peroxide.

Still other theories might be advanced, such, for example, as that the "polyprene sulfide" acts as a catalyst for the combination of sulfur with new rubber—but the five possibilities enumerated below are certainly the most logical for investigation:

- (1) Residual alkali in the reclaim
- (2) Unchanged accelerator in the reclaim
- (3) Depolymerization by the action of heat and mastication
- (4) "Head start" of the reclaim with respect to chemical state of cure
- (5) Oxidation products acting as curing agents

The experimental data presented in this paper are confined to work carried out to determine whether, and to what

<sup>20</sup> *J. Russ. Phys. Chem. Soc.*, **47**, 1453, 1462 and 1467 (1915); *J. Soc. Chem. Ind.*, **35**, 59 (1916).

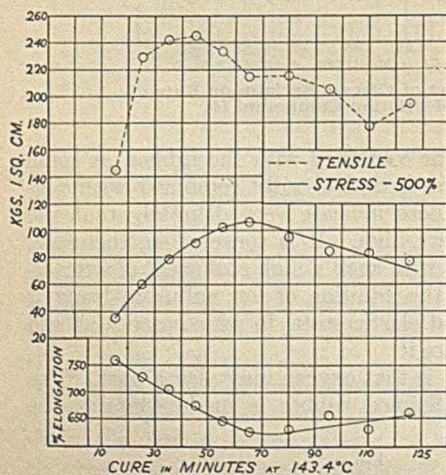


Figure 7—Compound X with No Additional Alkali

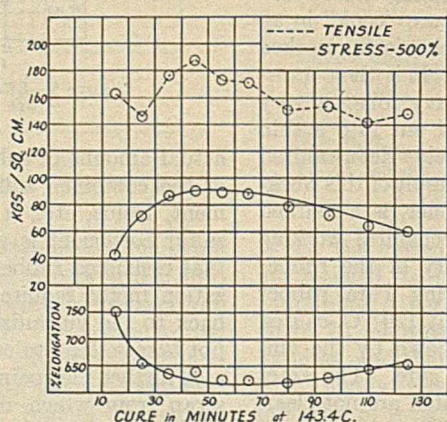


Figure 8—Compound IX Containing 39.5 Per Cent Whole-Tire Reclaim

Effect of Whole-Tire Reclaim vs. Added Alkali in Compound

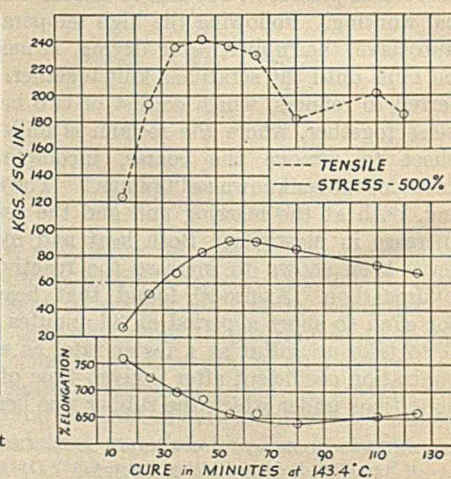


Figure 9—Compound X with 0.06 Per Cent NaOH to Rubber

extent, residual alkali, heat, and the chemical state of cure are responsible for the rapid curing rate of reclaimed rubber.

### Residual Alkali

Though the presence of alkali has previously<sup>10</sup> been advanced as the reason for the rapid rate of cure of reclaimed rubber, no conclusive data are available. With the purpose of settling this point, reclaimed rubber of known alkali content was used in compounding mixture IX. The sample of reclaim used was a whole-tire reclaim of the following composition:

	Per cent		Per cent
Acetone extract	10.60	Zinc oxide	10.0
Total sulfur	2.82	Clay	10.5
Free sulfur	0.07	Carbon black	6.0
Alkalinity (as NaOH)	0.10	Rubber content (by difference)	60.0
Ash	20.53		

On the basis of this analysis, a control compound, X, was made up containing no reclaimed rubber but all smoked sheets compounded with the pigments present in the reclaim together with the added zinc oxide, sulfur, and accelerator used in compound IX.

	IX	X
Smoked sheets	100	100
Reclaim	75	...
Sulfur	4	3
Di- <i>o</i> -tolylguanidine	1	0.7
Zinc oxide	10	12
Clay	...	5.5
Gas black	...	3
Liquid asphalt	...	4
	190.0	128.2

In order to show the effect of added alkali, three other compounds based on X were included. These contained, respectively, 0.06, 0.12, and 0.18 per cent of caustic soda to the rubber. The alkalinity of the reclaim (0.10 per cent) corresponds to 0.053 per cent of sodium hydroxide to the rubber in compound IX. Thus, the mixture containing no reclaim but 0.06 per cent of sodium hydroxide to the rubber was fully equivalent in alkali content to the mixture containing the reclaim. The alkali was added to these batches in the form of a 2.4 *N* solution; it was added to the batch toward the end of the mixing period after all the dry pigments had been thoroughly incorporated.

The results of this work are plotted in Figures 7 to 11. From these curves it is clear that, although the addition of 0.06 per cent of caustic did accelerate the cure of the new-rubber mixture, the rate did not equal that of the mixture containing 39.5 per cent of reclaim. This is clearly seen by comparing the time required in each case to reach the peak in stress at 500 per cent elongation. Even with

0.18 per cent of caustic to the rubber, which is more than three times that present in the mixture containing reclaim, the rate of cure is not equal to that of the mixture containing the reclaim.

Further proof that the alkali content of reclaim accounts at least only partially for the rapid rate of cure was obtained as follows: Scrap for use in reclaiming was made from quality tread XI and carcass XII. The tread was cured for 90 minutes at 143.4° C.; the carcass for 75 minutes at the same temperature. A 50:50 mixture of these two cured compounds constituted the scrap. This was then reclaimed in a small laboratory devulcanizer (Figures 12 and 12A),<sup>21</sup> consisting of a steel bomb 1.27 cm. thick with a capacity of 3.8 liters. It is shown in an inverted position, in which position it is operated. The charge consisted of 1 kg. of scrap and 2.2 liters of liquid. The heating was done electrically and a

total rubber in compound XIV. It is clear that there was no appreciable increase in rate of cure where the alkali reclaim was used, and that the addition of up to 0.12 per cent of alkali to the rubber did not materially affect the rate. This experiment is of interest as showing, not so much the effect of different concentrations of alkali, for the actual difference in the alkali content of the reclaims prepared by the two methods was very small, but as showing that the use of alkali in the cook does not bring about changes which appreciably affect the rate.

Action of Heat

In order to determine the extent, if any, to which the devulcanization temperatures are responsible for the rapid curing rate of reclaimed rubber, a series of experiments in the experimental autoclave was undertaken in which pale crepe was subjected to various temperatures, including that ordinarily used in devulcanization. Water was used as the heating medium. The pale crepe was a sample that had been thoroughly blended on a mill and then cut into small pieces in order to expose a large surface. One portion was subjected to a temperature of 93.3° C. for 6 hours; a second sample of this same rubber was heated at 137.7° C. for 6 hours; still a third was heated at 185° C. for 6 hours. To give a more complete picture of the behavior at 185° C., samples were also run at this temperature for 3 and for 9 hours, respectively. In Figure 15 are seen the results of compounding these different heat-treated samples in formula XV.

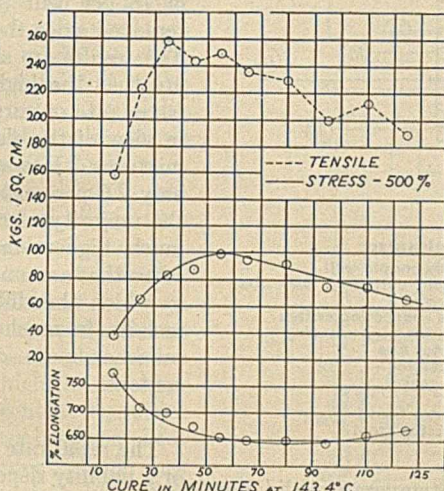
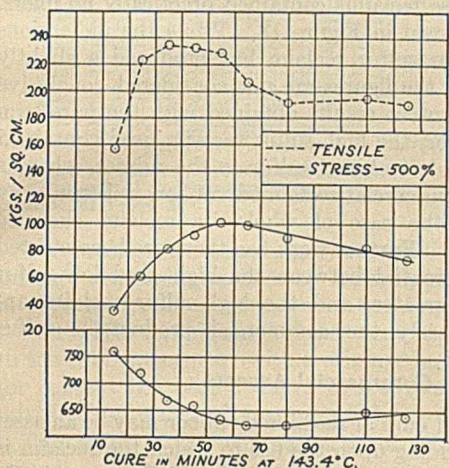


Figure 10—Compound X with 0.12 Per Cent NaOH to Rubber

Figure 11—Compound X with 0.18 Per Cent NaOH to Rubber

Effect of Whole-Tire Reclaim vs. Added Alkali in Compound X

moderate amount of agitation produced by mounting the bomb and furnace on a revolving support and providing a rocker arm, actuated by a motor-driven eccentric. With this autoclave reclaims could be made which duplicated very satisfactorily factory-scale products.

From the scrap described above, two separate batches of reclaim were made, using a 9-hour cook at 182–185° C. In one case the liquid used was water, and in the other 8 per cent caustic soda solution. The alkali cook, after washing, drying, and refining, showed an alkalinity of 0.01 per cent. These two reclaims were then used to the extent of 10 per cent in compounding a tread mixture quite similar to the tread used as scrap in manufacturing the reclaim, except that it contained 10 per cent of the reclaim. Compound XIII contains the alkali-cook reclaim, while compound XIV contains the water-cook product.

	XI	XII	XIII	XIV
Smoked sheets	53	100	57	57
Amber crepe	36	...	33	33
Rolled brown crepe	11	...	10	10
Water-cook-reclaim (50:50 XI and XII)	...	...	...	20.4
Alkali reclaim (50:50 XI and XII)	...	...	...	20.4
Sulfur	2.9	3	3.2	3.2
Di-o-tolylguanidine	0.7	0.5	0.7	0.7
Zinc oxide	36.5	2.75	32.5	32.5
Gas black	32.5	...	39	39
Mineral rubber	...	3.25	...	...
Pine tar	5.25	...	8	8
<b>Total</b>	<b>177.85</b>	<b>109.50</b>	<b>203.8</b>	<b>203.8</b>

	XV
Pale crepe	100
Sulfur	3
Zinc oxide	3
Di-o-tolylguanidine	0.5
<b>Total</b>	<b>106.5</b>

A sample of this same pale crepe, which had been soaked in water for 24 hours at 60° C., was also included. The water extract of the pale crepe was 2.63 per cent; after soaking at 60° C. the extract was 1.35 per cent. From Figure 15 it appears that this soaking increased the rate of cure of this rubber—why, the writers do not know. A somewhat similar increase in physical properties and rate of cure has been recorded without explanation by van Heurn.<sup>14</sup> From these curves it is clear that by keeping the time of treatment constant (6 hours) and increasing the temperature, there resulted little or no change in rate of cure as judged by the optimum in the curves. The higher the temperature, the lower was the modulus. If anything, the sample of rubber which was subjected to a temperature no higher than 60° C. has the fastest rate of cure; hence, it would appear that the high temperature used in devulcanization plays a very small part in the rapid rate of cure of reclaimed rubber. Considering the curves which represent the three different time intervals of heating at 185° C., it is interesting to note that after 3 hours' heating there was practically no change in the modulus obtained or in the rate of cure.

It is worthy of note in connection with the tensile-strength results shown in Figure 16 that up to 137.7° C. the heat treatment had very little effect on the tensile strength of the rubber, while the rubber subjected to a temperature of 185° C., even for 3 hours, lost appreciably in tensile strength.

In Figure 13 are plotted the modulus curves of the two mixtures (XIII and XIV). Figure 14 gives curves showing the influence of 0.06 and 0.12 per cent of caustic soda to the

<sup>21</sup> Designed by Roy W. Brown, of the Firestone Engineering Laboratory.

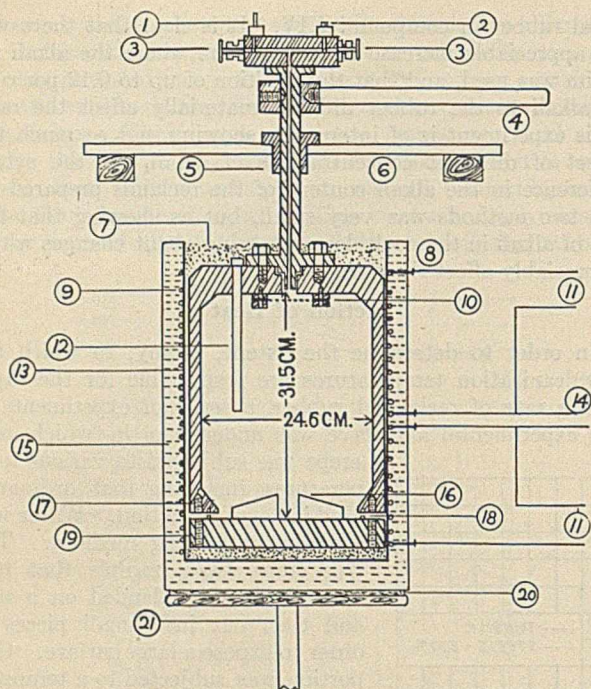


Figure 12—Experimental Devulcanizer

- |   |                                      |
|---|--------------------------------------|
| 1—Blow-off line                           | 12—Thermocouple well                 |
| 2—Pressure-gage connection                | 13—Copper cylinder, asbestos-covered |
| 3—Valves                                  | 14—Series connection switch          |
| 4—Rocker arm                              | 15—Magnesia pipe covering            |
| 5—Bearing                                 | 16—Agitator fins                     |
| 6—Support                                 | 17—Bolt circle                       |
| 7—Asbestos fiber                          | 18—Lead gasket                       |
| 8—Electrical connection                   | 19—Lid                               |
| 9—Chromel-wire heating element            | 20—Asbestos board                    |
| 10—Removable screen                       | 21—Revolving stool                   |
| 11—Alternating-current source (110 volts) |                                      |

Three and 6 additional hours at this temperature did not lower the tensile figures. Winkelmann,<sup>3</sup> working with a vulcanized tread compound, found that the decrease in tensile had reached a maximum in 4 hours or less at 135° C.

#### Influence of Combined Sulfur

If there is anything to the theory that the rapid rate of cure of reclaimed rubber is connected with its chemical "head start" then the combined-sulfur content of a reclaim should be an important factor in the rate of cure. In order to throw light upon this point, scrap for reclaiming was made from the two following compounds, which differ only in sulfur content:

	XVI	XVII
Smoked sheet	100	100
Sulfur	3	1.5
Zinc oxide	2	2
Magnesium oxide	2	2
Tetramethylthiuram disulfide	0.27	0.27
	107.27	105.77

Each compound was cured for 20 minutes at 132.2° C. and then comminuted to the approximate size of ordinary whole-tire scrap and heated in the experimental devulcanizer in water for 8 hours at 185° C. The respective reclaims were then dried and refined in the usual manner. These reclaims, which had a combined-sulfur content of 2.5 and 1.4 per cent, respectively, were tested in two types of compound, a pure gum (XVIII) and a tread (XIX).

	XVIII	XIX
Smoked sheets	100	100
Sulfur	3	2.5
Zinc oxide	5	14
Di-o-tolylguanidine	0.7	0.7
Gas black	...	40
Clay	...	3
Pine tar	...	7
	108.7	167.2

Using XVIII as the control, two mixtures were made up in which 27.2 parts of the smoked sheets were replaced by the respective reclaims. This gave a reclaim content of 25 per cent. Since the pigmentation of these special reclaims was very low, no allowance was made for their pigment content. Figure 17 shows the load required to produce an elongation of 500 per cent over a range of cures. It is seen that the peak in each curve occurs at the 60-minute cure at 143.4° C. Both compounds containing the reclaim are much stiffer than the compound containing all new rubber. This is typical of the effect of reclaimed rubber on modulus. The above results have been checked, so apparently the combined sulfur of the reclaim had very little to do with the rate of cure.

When these reclaims of different combined-sulfur content were introduced into tread compound XIX to the extent of 18 per cent (30 parts), an equal weight of rubber was removed since these reclaims contained practically no fillers. The results are shown in Figure 18. While the indications are that the higher sulfur reclaim has produced a slightly faster rate of cure, the figures are not considered conclusive in view of the clean-cut results obtained with the pure-gum mixtures. However, the high-sulfur reclaim used contained only 2.3 per cent of combined sulfur to the rubber, whereas the majority of commercial reclaimed rubbers will run very much higher—in the case of whole-tire reclaim close to twice that amount. Further work has therefore been started in which the differential between the high- and low-sulfur reclaim is much greater, and the high-sulfur reclaim approaches more closely the commercial product in sulfur content.

#### Commercial Aspects

The rapid rate of cure of reclaimed rubber may be an asset or a liability depending upon the use to which the reclaim is to be put. Inasmuch as accelerators are added to practically all commercial rubber mixes to hasten the cure, it would seem to be a very desirable property. However, where rapid rate of cure is desired and obtained through the use of accelerators, it is usually controllable; this is not always the case, but by reducing the concentration of most accelerators the rate may be reduced, and if this is not effective, as in the case of certain of the ultra-accelerators like the tetramethylthiuram mono- and di-sulfides, the concentration of sulfur may be reduced.

In mixtures containing any appreciable amount of reclaim such changes are quite ineffective, as Winkelmann<sup>3</sup> has pointed out. In Figure 19 are plotted data showing the effect of reducing to the extent of 10 per cent the sulfur in pure-gum formula II. This reduction from 3.0 to 2.7 per cent of sulfur to the rubber produced no shifting of the peak but simply lowered the modulus curve. Figure 20 shows the effect of making a greater percentage reduction of sulfur in the highly compounded mixture VIII. Here the sulfur to rubber (new rubber plus rubber in reclaim) was reduced

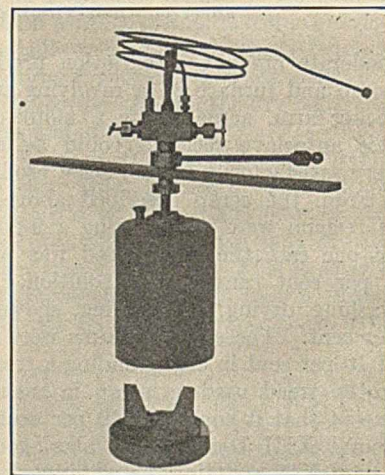


Figure 12A—Experimental Devulcanizer

from a total sulfur (added sulfur plus total sulfur in the reclaim) of 3.58 per cent to a total sulfur of 2.70 per cent, which is a reduction of 24 per cent. The new sulfur added in one case was 2.8 per cent to the rubber, in the other 1.8 per cent, or a reduction of 35.7 per cent. While this very

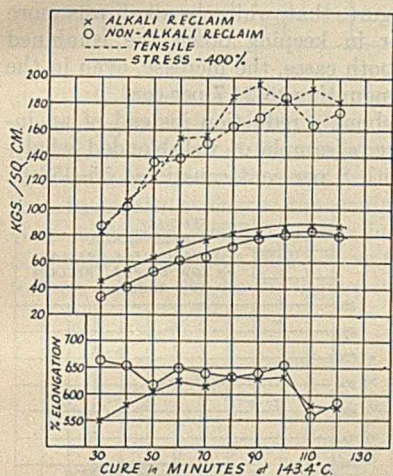


Figure 13—Effect of 10 Per Cent Alkali and Non-alkali Reclaims in Tread Compounds XIII and XIV

The futility of attempting to reduce the rate of cure of a mixture containing reclaim by reducing accelerator is shown in Figure 21. The curves cover the data obtained on compound VIII, containing 0.97 per cent of di-*o*-tolylguanidine to the rubber, together with a mixture in which the accelerator content has been reduced to 0.45 per cent and another mixture from which all organic accelerator has been removed.

The result of this characteristic of retaining rate of cure regardless of sulfur or accelerator concentrations is that it is extremely difficult, in using reclaimed rubber, to balance the cure in the various parts of a thick article. For example, in a pneumatic tire the carcass must have a much faster curing rate than the tread, for the tread, especially on the outside, gets much more heat during vulcanization than the

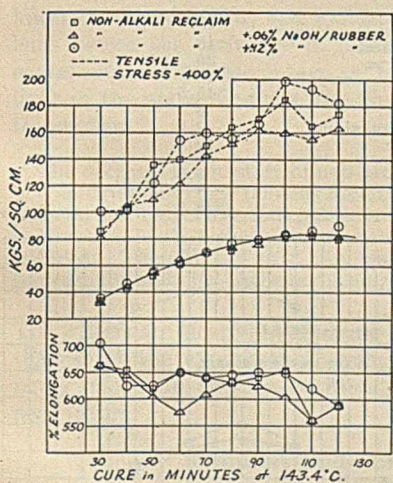


Figure 14—Effect of Added Alkali on Tread Compound XIV

standpoint of curing rate. On the other hand, when reclaim is added to a tread mixture the rate becomes so fast that in order to vulcanize the tread properly the temperature or duration of the curing period must be reduced to such an extent that it becomes difficult to cure the carcass properly. A remedy is, of course, to speed up the carcass through the use of ultra-accelerators, but this makes it very

difficult to process the fabric as the curing rate of the skim compound is such that premature vulcanization or "scorching" is liable to occur during the calendaring operation, ruining the processed fabric.

As a result many tires on the market today containing reclaim are seriously overcured with respect to the tread. And this is not always incidental to the use of reclaim. It seems to be the practice of some to use a high-sulfur ratio in their recipes which have a high reclaim content in order to increase the tensile strength. A "full" cure always improves tensile properties whether a stock contains reclaim or not, but experience has, or should have, taught the rubber technologist to keep his products below the state of optimum properties when freshly cured, for otherwise they suffer distinctly after a period of aging. The temptation to use high sulfur in the case of compounds containing reclaimed

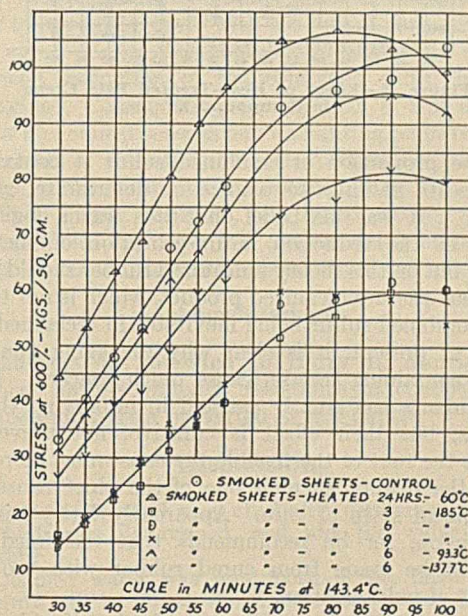


Figure 15—Effect of Heat-Treated Pale Crepe in Compound XV

rubber is great, for appreciable amounts of reclaim lower tensile strength and it is one of the technologist's problems to remedy this.

Of equal, if not greater, importance is the problem of maintaining the physical properties during aging. It has already been pointed out that the percentage of combined sulfur in reclaim is high. When this is used in compounding and undergoes a second vulcanization, the combined sulfur is still further increased. It has been shown<sup>22</sup> that the combined sulfur or chemical state of cure is no criterion of initial physical properties, but it is certain that no rubber technologist is unaware of the detrimental influence of high chemical state of cure on the aging properties of soft-rubber products. The trend toward low-sulfur, non-blooming compounds has been chiefly due to the better aging obtained with such compounds provided they are properly cured, and only secondarily to a desire to improve the appearance through eliminating the unsightly sulfur bloom from the surface.

To how great an extent the technologist's views on this question of the influence of chemical state of cure on the stability of rubber products have changed is shown in the following quotation from C. O. Weber:<sup>4</sup> "It is well recognized that the higher we vulcanize India-rubber—i. e., the

<sup>22</sup> Shepard and Krall, *Ind. Eng. Chem.*, **14**, 951 (1922).

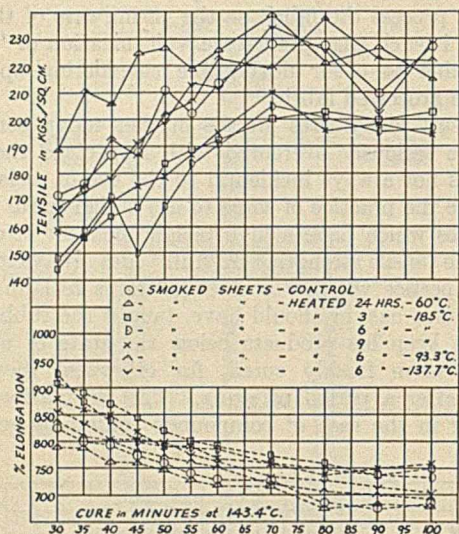


Figure 16—Effect of Heat-Treated Pale Crepe in Compound XV

higher the proportion of combined sulfur it contains, the smaller is its liability to oxidize or deteriorate, generally speaking.<sup>23</sup> It was his belief that this was a logical consequence of the reduction in unsaturation of the rubber molecule, but on this theory vulcanized rubber should be more stable than the unvulcanized product, which is not the case.

High combined sulfur being inevitable in reclaimed rubber as made at present, it is clear why the aging qualities of products containing reclaim cause much concern. The use of antioxidants has greatly assisted in improving the aging properties, but their effect is curative, not preventative. To get at the root of the trouble the cause must be removed, and in the writers' opinion one of the chief causes is the high chemical state of cure. Apparently Boiry<sup>23</sup> is of the same opinion, for he recommends that reclaimed rubber should not be made from cured rubber with too high a coefficient of vulcanization.

Removal of the chemically combined sulfur in reclaim has never been accomplished without subjecting the rubber scrap to such deep-seated changes that the product is commercially valueless.<sup>23,24</sup> Present methods of alkali reclaiming are such that, though some

of the free sulfur in the scrap may be removed by the alkali during the process, the combined sulfur is actually increased (Table II), probably because the high temperatures used combine a part of the free sulfur before it is removed by the alkali. Ways and means of preventing this become increasingly important as reclaimed rubber is "re-reclaimed." In order to prove whether reduction of the combined sulfur in reclaim really does mean anything from an aging standpoint, experiments were carried out using tread compound X cured 90 minutes at 143.4°C. as scrap for reclaiming. The results are shown in Table II.

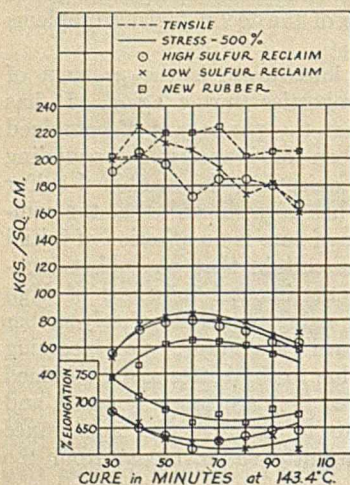


Figure 17—Effect of 25 Per Cent of High- and Low-Sulfur Reclaim on Pure-Gum Compound XVIII

ing tread compound X cured 90 minutes at 143.4°C. as scrap for reclaiming. The results are shown in Table II.

<sup>23</sup> Rev. gén. caoutchouc, Spec. No. (Livre d'Or), 205 (January, 1927).

<sup>24</sup> Alexander, Chem.-Ztg., 36, 1289, 1340, 1358 (1912).

Table II—Effect of Reclaiming on Combined-Sulfur Content

	FREE SULFUR Per cent	TRUE COMBINED SULFUR <sup>25</sup> Per cent	TOTAL SULFUR Per cent
Original scrap	0.64	0.93	1.68
Water cook	0.13	1.31	1.73
8% caustic cook	0.14	1.16	1.67

It is clear from these figures that, while the alkali was more effective than the water in keeping down the combined sulfur, the value rose in both cases, the increase, even in the case of the alkali cook, amounting to 24.7 per cent.

In an effort to bring about a reduction instead of an increase in combined sulfur, a sample of well-blended whole-tire scrap was treated with 8 per cent caustic at 55–65°C. for 60 hours to remove free sulfur; at the end of this pretreatment the alkaline liquor was decanted and the scrap thoroughly washed. It was then devulcanized according to the usual procedure, using 8 per cent caustic for 9 hours at 183–184°C. As a control another sample of the same scrap was devulcanized without this pretreatment. The analytical results on these two samples are given in Table III.

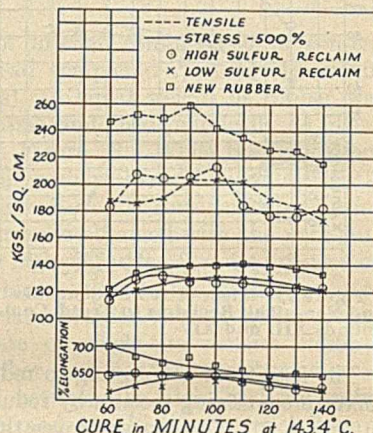


Figure 18—Effect of 18 Per Cent of High- and Low-Sulfur Reclaim on Tread Compound XIX

Table III—Effect of Pretreatment on Combined-Sulfur Content of Reclaim

	FREE SULFUR Per cent	TRUE COMBINED SULFUR Per cent	TOTAL SULFUR Per cent
Without pretreatment at 60°C.	0.19	1.82	3.07
With pretreatment at 60°C.	0.18	1.29	2.45

The result of this pretreatment was thus a reduction in combined sulfur of 29.1 per cent. These two reclaims were then used in compounding tread XX in which the reclaimed rubber amounts to 20 per cent.

XX	
Smoked sheets	48
Amber crepe	39
Rolled brown crepe	13
Reclaim	45.5
Sulfur	3.3
Di-o-tolylguanidine	0.9
Zinc oxide	15.5
Gas black	56
Pine tar	6.8
228.0	

Table IV shows the physical properties of the resulting compounds when cured for 80 minutes at 143.4°C. (best aging cure), both when freshly cured and when aged in the dark for 1 year, artificially aged for 8 days at 70°C., and for 27 and 36 hours, respectively, in the oxygen bomb at 60°C. (300 lbs. pressure of oxygen). Heat aging for 8 days

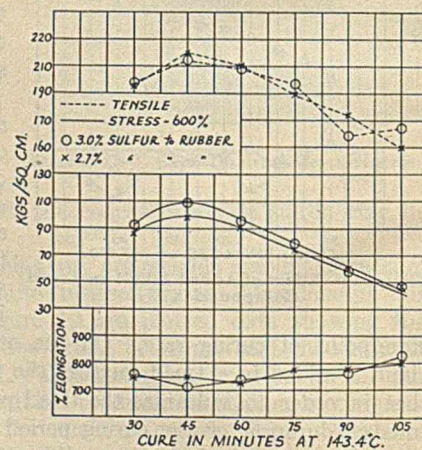


Figure 19—Effect of Reducing Sulfur Concentration in Compound II

<sup>25</sup> Kelly, Ind. Eng. Chem., 14, 196 (1922).



Table IV—Tensile Strength of Tread Compound XX, Cured for 80 Minutes at 143.4° C.

TRUE COMBINED SULFUR CONTENT OF RECLAIM	FRESHLY CURED	1 YEAR NATURAL AGING		8 DAYS AT 70° C.		IN OXYGEN BOMB			
		Actual	Change	Actual	Change	27 HOURS AT 60° C.		36 HOURS AT 60° C.	
						Actual	Change	Actual	Change
Per cent	Kg./sq. cm.	Kg./sq. cm.	Per cent	Kg./sq. cm.	Per cent	Kg./sq. cm.	Per cent	Kg./sq. cm.	Per cent
1.28	191	135	-29.3	139	-27.2	112	-41.3	99	-48.2
1.82	185	126	-31.9	136	-26.5	90	-51.3	88	-52.4

at 70° C. failed to differentiate appreciably these stocks, while oxygen-bomb aging for long periods showed up definite differences in favor of the compound containing the reclaim of lower combined-sulfur content. While this lost 41.3 per cent in tensile strength, the compound containing the reclaim of higher combined sulfur lost 51.3 per cent; the loss of the latter was thus 24.4 per cent greater than that of the former. After 36 hours' aging in the oxygen bomb the

mechanical working is responsible for the rapid rate, the experimental data obtained by subjecting new rubber to devulcanization temperatures do not support this.

From the data presented it appears that the chemically combined sulfur in reclaim is not an important factor in the rate of cure. This point is being further investigated, as is also the influence of residual accelerator, and of oxidation products.

While the amount of combined sulfur in reclaimed rubber appears to have little to do with the rate of cure, its influence on the aging qualities of compounds containing reclaim is pronounced, reduction in the combined sulfur leading to better aging. Consequently the problem of true devulcanization in a chemical sense is one warranting renewed interest.

As a result of this study of reclaimed rubber, the writers are led to the conclusion that in compounding with reclaimed rubber it is highly desirable, and quite necessary from an aging standpoint, to use a low concentration of sulfur, and to reduce either the time or temperature of vulcanization.

#### Acknowledgment

The authors are indebted to Harry L. Morris, of this laboratory, for his valuable assistance in connection with the compounding data presented in this paper.

#### Discussion

Q. By what method was alkalinity determined, how was sodium hydroxide determined, and was the water used free from alkali?

A. Distilled water was used both in the devulcanization experiments and in the alkalinity determinations. This water was neutral, as determined by ordinary indicators.

The method of determining alkalinity was as follows:

The sample was sheeted to 0.005 inch thickness, and 100 grams of this were boiled vigorously in distilled water for 3 hours, thereupon removed, the adhering liquid squeezed out by hand (the operator using rubber gloves free of any trace of alkali), and the sample given four rinsings and squeezings with hot distilled water. Thereupon the sample was redigested for 2 hours, the rinsing process being repeated. All the extraction liquors were combined and titrated to neutrality with *N* sulfuric acid using methyl red as indicator. The total alkalinity is given as per cent NaOH.

Q. It has been found that by very long extractions, up to as high as 48 hours, the alkali content increases up to 0.5-1 per cent. The question is whether all alkalinity was determined as above.

A. We have found that in two subsequent digestions very small amounts of alkaline material were further extractable—

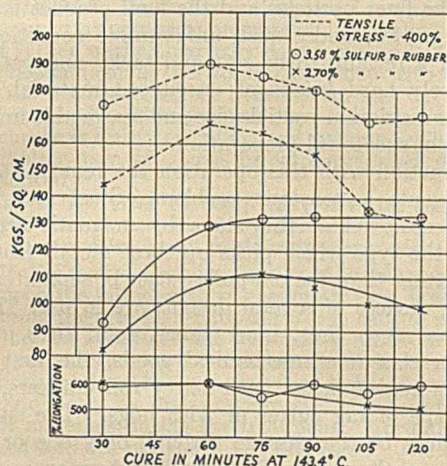


Figure 20—Effect of Reducing the Sulfur Concentration in Compound VIII

difference was 8.7 per cent. Natural aging brought out a difference in percentage deterioration of 8.9 per cent. These figures point definitely to the superiority of the reclaim of lower combined sulfur, and indicate clearly one of the problems before the reclaimer in making a reclaim from scrap containing a high percentage of reclaimed rubber. In the light of the above findings, the views of Weber<sup>4</sup> are subject to question:

The decrease in the state of non-saturation of the India rubber in a soft rubber article remains intact in the subsequent recovery process, and on revulcanizing this recovered rubber the unavoidable result is that the state of non-saturation is still further reduced. The effect of this, as a matter of course, is to greatly increase the stability of the revulcanized recovered rubber.

The writers are at present studying this problem, and through the use of the experimental devulcanizer described in this paper expect to be in a position to publish on this in the near future.

#### Summary and Conclusions

The rapid rate of cure of reclaimed rubber, while undoubtedly influenced by the alkali used in the reclaiming process, is only partially attributable to the presence or influence of alkali. Not only is this clearly shown by the experimental data, but by the fact that reclaimed rubber prepared in the absence of alkali, though slower curing, is still much faster in curing rate than new rubber.

In spite of the plausibility of the theory that depolymerization or disaggregation under the influence of heat and

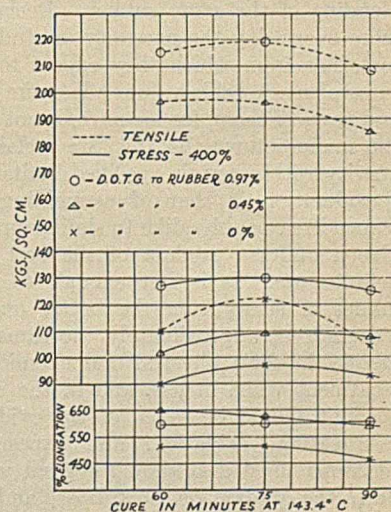


Figure 21—Effect of Reducing Accelerator Concentration in Compound VIII

about 0.002 to 0.004 per cent per digestion. The method used is satisfactory for comparative tests. Assuming that further small amounts of alkali were present, however, the

data presented are all the more conclusive that residual alkali accounts in only a small measure for the rapid rate of cure of reclaimed rubber.

## Factors in Processing Reclaimed Rubber

P. S. Shoaff

THE GOODYEAR TIRE AND RUBBER CO., AKRON, OHIO

Production of reclaimed rubber of uniformly good physical and chemical properties is dependent first upon judicious classification and blending of raw materials. Grinding to a state in which no large particles are present, but without an excess of fines, allows a minimum devulcanizing time at a given temperature, decreases the tendency to depolymerize to an objectionable extent, and reduces the requirement for softeners. These conditions facilitate further processing to a smooth product of good quality with the desired plasticity and with optimum compounding, milling, calendaring, and tubing characteristics. Devulcanization at high temperatures tends to reduce the tensile slightly and to increase the elongation as compared with treatment at lower temperatures. Alkali reclaimers require efficient washing to remove residual caustic and the recovery of fines from the wash liquors involves problems of settling and filtration or screening. Drying of wet-processed reclaims at high temperatures or for an excessively long time results in tacky products, just as does over-devulcanization. A minimum amount of milling and refining at normal temperatures is desirable to preserve the quality, therefore previous processing should be thorough and uniform.

Some comparisons of types of equipment are made and some desirable future developments are discussed.

IN ANY discussion of the factors especially influencing the manufacture of reclaimed rubber with optimum physical and chemical properties there naturally arises first the problem of the proper classification, selection, and blending of the scrap rubber. Reclaimers are appreciating more every day the necessity of studying the nature of the materials from which they expect to obtain rubber substitutes of marketable value. The aim in blending scrap tires and parts of them, for instance, is not merely that of assuring the manufacturer that his tire reclaim will have a specific gravity within certain specified limits. The more important consideration is that of assembling materials which will respond reasonably alike to similar processing and which will give a uniform product of the best possible quality for a definite use. It is not enough to segregate the cheaper grades of scrap from the better ones. Even similar raw materials of approximately the same original quality vary greatly in their physical and chemical state owing to age, treatment while in use, and in the case of tires especially, account should be taken of the evident deterioration from overheating, oxidation, and exposure to sunlight. The reclaimer must also allow for great variations in the toughness, the proportion of rubber, and state of cure of the vulcanized materials.

### Grinding

In rubber-reclaiming processes the preparation of raw materials has certainly as important an influence upon succeeding treatments and the ultimate character of the product as it exerts in most manufacturing operations requiring grinding and sizing. It is desirable to reduce

vulcanized scrap to a certain maximum particle size and yet not to produce an excessive proportion of fines. If considerable oversize is present, the time of devulcanization and the extent of milling and refining must be increased in order to reduce these large particles to the proper state. In that case there is a tendency for an abnormal depolymerization of the finer particles and the final product is inclined to be tacky. So, under such unfavorable conditions, it is possible for a reclaim to be soft and tacky and yet contain comparatively hard lumps of unreduced material. Therefore, proper maximum particle size and reasonable uniformity are criteria of successful preparation.

In conjunction with this operation the removal of tramp metals presents a constant problem. Steel and iron are fairly well removed at this stage by magnetic separators, preferably the type which picks up these metals from a belt conveyor rather than the old pulley style of separator.

Grinding devices of several designs are in use. For such materials as scrap tires, inner tubes, solid tires, air bags, and certain classes of mechanical goods, the first step in reduction is accomplished with heavy roll crackers, or with a sturdy type of rag cutter or with hogs. The succeeding operation may be the passage through only one or a series of crackers or through a fine grinding hog or a shredder. Usually continuous screening is necessary to obtain the best conditions. Following the first cutting or chopping operation, units consisting of a single cracker and a screen with a continuous return of oversize to the cracker give very good results. Choice of grinding equipment should be based not only upon mechanical and production efficiencies and upon the requirements previously pointed out, but also upon an appreciation of the advantages of subjecting most scrap rubber to a crushing action in order to facilitate the succeeding treatments.

### Power Requirements for Grinding Representative Scrap Vulcanized Materials under a Particular Set of Conditions

MATERIAL	FINISHED RECLAIM Kilowatt-hours per lb.
Debeaded black tires	0.11
Inner tubes	0.19
Solid tires, air bags, etc. (high gravity)	0.16

In preparing vulcanized scrap containing cotton fabric it is frequently suggested that the fiber be removed in the course of the grinding operation so that there will consequently be required a proportionately less quantity of caustic soda in the devulcanizing process. So far no means have been found for effecting a complete separation; fine particles of rubber adhere to the disintegrated fabric, with the result that too much rubber is lost and the value of the fiber itself is lessened. The impure fiber is worth less than linters and it cannot stand the cost of recovery. Neither will the saving in caustic justify the expense of complete separation.

### Devulcanization

The so-called devulcanization of cured scrap rubber is the most important step of the reclaiming process. It challenges

the interest of the chemist and the engineer and is the field whence the principal future developments must come if there is to be any great improvement in the properties of reclaimed rubber. Several methods are employed dependent upon the nature of the raw material.

**FABRIC-FREE MATERIALS—Direct Steam Heater and Pan Process.** This method is popular in devulcanizing scrap inner tubes, solid tires, air bags, and similar materials, especially when it is not deemed necessary to remove the free sulfur by digestion in caustic soda solution. Usually the ground scrap is first mixed with softening agents and is then loaded into steel boxes. These are stacked on cars with covers over each container or over the top of the stacks, and the charge is run into a cylindrical heater, similar to an inner-tube vulcanizer. The treatment consists in heating the charge directly with live steam usually under pressures of from 75 to 125 pounds. The heating period will vary from 8 to 30 hours according to the character of the material. The softened stock is then milled and refined.

**Heater Process with Agitation.** Sometimes it is desired to remove the free sulfur from fabric-free scrap and then to follow with the heater method. In that case the ground scrap is digested for several hours at atmospheric pressure in a hot solution of caustic soda. It is then washed, partially dewatered, and charged into a jacketed heater (usually horizontal) provided with an agitator. Most of the residual moisture is driven off and devulcanization is then obtained under pressure by indirect heating. The finished charge is ready for milling and refining. The same type of devulcanizer may, of course, be employed when desulfurizing is not practiced.

This fabric-free class of scrap may also be simultaneously desulfurized and devulcanized by the alkali process and considerable tube reclaim is still made in that manner.

**The Alkali Process—Devulcanization of cured rubber materials containing cotton fabric, such as pneumatic tires, is accomplished by subjecting them to high temperatures in caustic soda solution in steam-heated digesters—the well-known alkali process.**

Two types of digesters or devulcanizers are in use, the vertical and the horizontal. These machines are jacketed for heating the contents indirectly by high-pressure steam. Agitators mix the charges of materials during the treatment. Certain advantages are claimed for both designs of devulcanizers. The vertical machines require barely half the floor space occupied by the horizontal devulcanizers of equal operating capacity. It is easier to obtain more efficient mixing in the horizontal type, since the action of the agitators carries upward the heavier particles of the contents which tend to settle to the bottom and the floating material is continuously swept down into the bulk of the charge. However, with efficiently designed agitators and proper speeds a homogeneous mixing is obtainable in either case.

The size of the charge must be proportioned with the view of insuring the best agitating and heating effects. The average charge for a 2000-gallon vertical devulcanizer is about 3500 pounds of ground scrap tires and 1100 gallons of caustic solution. The horizontal machines are usually 6 feet in diameter and have a capacity of approximately 3000 gallons; they take charges of about 5000 pounds of similar material and 1600 to 1800 gallons of caustic solution.

The ground scrap with the necessary quantity of caustic soda solution is charged into a digester, softeners are added, if desired, and the mixture is heated for a specified time. The proper treatment in the devulcanizing operation results in the conversion of the cotton fiber to soluble hydrocellulose, the removal of nearly all the free sulfur, and the plasticizing of the rubber. The first effect of the high temperature is to cause a small amount of the original free sulfur to combine with the rubber; in other words, there is an incipient vulcanization at the start of the process of devulcanization.

Typical Conditions in Reclaiming Debeaded Black Tires

STEAM PRESSURE Lbs.	APPROX. TEMPERATURE ° F.	HEATING TIME Hours	NaOH PER 100 LBS. SCRAP Lbs.
125	353	24 to 36	130 to 140
150	366	14 to 20	130 to 135
195 to 200	385 to 388	8 to 14	125 to 130

The strength of the caustic solution will vary from 4 per cent to 6 per cent; the higher the temperature employed, the lower the caustic strength required. Destruction of the fabric is effected in 7 to 8 hours from the beginning of the heating period when the highest temperature is used, in 10 to 14 hours with 150 pounds steam, and in 18 to 24 hours with 125 pounds steam. If softeners are added, the plasticizing time, and, therefore, the total time, is usually in the lower range given in the table.

In devulcanizers of the types described containing approximately the charges mentioned and heated with steam at 195 to 200 pounds pressure, about 1½ hours are required to raise the temperature of the contents to 350° F. and it is nearly 4 hours before a temperature near that of the jacket steam is reached.

Comparative steam requirements for devulcanization of the classes of scrap in question by the various methods are shown in the following table:

Steam for Devulcanization		LBS. STEAM PER LB. FINISHED PRODUCT
MATERIAL	PROCESS	
Black tires	Alkali	1.40
Inner tubes	Heater (either type)	0.80
Solid tires, air-bags, etc.	Heater and pan	0.70

L. E. Weber<sup>1</sup> considers devulcanization as fundamentally a process of depolymerization and suggests that, if vulcanization is a polymerization, then the step in reclaiming cured rubber called "devulcanization" is properly termed, since it is to a large extent a reversal of the changes which occur in vulcanization. However, the theory has been advanced that physical disintegration rather than depolymerization may be the chief factor involved. Maximoff<sup>2</sup> holds that the mechanical plasticizing of raw rubber is one of mechanical disintegration rather than of depolymerization. Since plasticizing is an essential effect of devulcanization, it might be inferred that the devulcanizing process is just an extension of the breaking-down process, purely physical and not involving depolymerization. But it is pointed out that devulcanization imparts plasticity to a material lacking that property and that it is not a modification or continuation of an existing property. Maximoff assumes that the plasticizing of raw rubber is a result of the solution of the solid phase in the liquid phase and that devulcanization of cured rubber represents changes in the insoluble solid phase which is unstable at high temperatures. It is generally accepted that the principal effect of the heat treatments which we have reviewed is that of depolymerization.

Winkelmann,<sup>3</sup> Boiry,<sup>4</sup> and others have called attention to the deteriorating action of high temperatures incident to the present reclaiming methods and have advanced opinions on the mechanism of devulcanization. The connection between the amount and nature of the chloroform extract from acetone-extracted reclaimed rubber and the extent of its devulcanization seems to throw some light on the question. At least it appears that the chloroform extractable constituents are a measure of depolymerization or disaggregation and of plasticity. The extremely low viscosity of the chloroform extract is mentioned as evidence that it is composed of hydrocarbons in a low state of polymerization. Prolonged heating in devulcanization at the temperatures employed increases the chloroform extract while the acetone extract and the sulfur in the former change unnoticeably.

Devulcanization to the same apparent state of smoothness of the finished product at higher temperatures gives a reclaim with slightly lower tensile and a little higher elongation than that obtained at lower temperatures.

With continued heating at the temperatures necessary in present methods the effect of depolymerization is also evidenced by an increase in plasticity and tackiness. Whitby<sup>5</sup> gives some of his own observations and comments upon the findings of Fickendey, Corter, Henri, Bernstein, and Van Rossem on the subject of tackiness of raw rubber. It is concluded that depolymerization or disaggregation is the fundamental cause but that the presence of oxygen is essen-

<sup>1</sup> "The Chemistry of Rubber Manufacture," p. 263.

<sup>2</sup> *Caoutchouc & gutta-percha*, 24, 13,582 (1927).

<sup>3</sup> *Ind. Eng. Chem.*, 18, 1165 (1926).

<sup>4</sup> *Rev. gén. caoutchouc*, Spec. No., 205 (January, 1927).

<sup>5</sup> "Plantation Rubber and the Testing of Rubber," p. 100.

tial, that it has a catalytic influence on the depolymerization, and that the latter would not occur appreciably in its absence.

In devulcanizing cured rubber there are usually employed softening agents such as pine tars or pine oils, coal tar or pitch, mineral oils, asphalt-base softeners, etc. The tendency is to reduce the proportion of such agents and to eliminate their use entirely. If too much dependence is put upon their action for the purpose of assisting in making a "smooth" reclaim, the incorporation of the product in rubber compounds will give stocks that are troublesome in milling, calendaring, and tubing operations. Since certain softeners promote good aging characteristics while others exert a deteriorating influence, their value should be gaged even more from these considerations than from their effects as plasticizers.

#### Washing Alkali Reclaims

The liquors in a finished charge from a devulcanizer, in which scrap tires, for example, have been treated by the alkali process, in addition to other varying constituents in solution or in suspension, contain sulfides and polysulfides and a certain amount of residual caustic soda which must be removed by washing. The soluble sulfur compounds are objectionable and it is well known that caustic in appreciable amounts renders the reclaim a dangerous material in a rubber stock owing to its action as an accelerator of vulcanization. A safe condition is a relative maximum content of 0.10 per cent sodium hydroxide as indicated by titration of a 4-hour boiling water extract of a 10-gram sample. The actual total alkalinity is determined by titration of no less than a 48-hour water extract. With continued extraction with hot water whole-tire reclaim may show a total alkalinity of 0.5 to 0.75 per cent where the ordinary test as reported in analyses may still be under 0.1 per cent.

When the caustic content of the liquors is appreciable—over 0.5 per cent NaOH, for instance—it is usually profitable to recover them and to use them as the base for fresh solutions for succeeding charges. In these cases the recovery of the weak solution is necessarily only partial and is effected by screening the entire contents of the devulcanizers. In systems using 195 to 200 pounds of steam the liquors normally contain about 0.5 per cent of sodium hydroxide and with pressures of 125 to 150 pounds the caustic content is about 0.7 to 1.0 per cent.

Various methods of washing the devulcanized materials are in vogue. In some instances it is flushed into large tanks and alternately washed and drained. Continuous screens and stationary, inclined screens are common. The continuous rotary washer performs this operation very successfully in several plants. It is simple, efficient, and requires little attention.

Efficient washing to a degree such that the finished reclaim will show an apparent alkalinity content below 0.10 per cent usually requires about  $2\frac{1}{4}$  gallons of water per pound of product.

Previous to the washing operation it is often the practice to remove as much as possible of the non-magnetic tramp metal and such other foreign matter as small rock particles in "jigs" or on riffle tables. The presence of such impurities interferes with refining as well as being objectionable in the finished product.

**RECOVERY OF FINES FROM WASH WATERS**—The recovery of the fine devulcanized rubber from the wash waters presents another interesting chemical engineering problem. For every 1000 pounds of devulcanized material there is as much as 1500 gallons of this water with a content of about 1.0 per cent by weight of solids. In some cases the entire volume of wash water is sent direct to save-all screens, but

lately there have been applied the settling and filtration principles frequently met in the general chemical industry. Continuous thickeners function well in the first step of concentration. About 85 per cent of the solids are easily settled and the remainder will float owing to the presence of air bubbles. The floating stock is skimmed off and added to the main sludge pumped from the bottom of the thickener.

The sludge mixture will normally contain 6 to 8 per cent of solid material. This is usually recovered either with continuous screens or with continuous rotary filters. An efficient filtering device will discharge the solids with 60 to 65 per cent moisture. The recovered material is added to the main bulk of stock just previous to the drying operation.

#### Dewatering

In the alkali process partial dewatering is done by continuous screw presses or centrifugals. The material delivered to the equipment may have a water content as high as 85 per cent. Efficient screw presses will reduce the water to 30 to 35 per cent. The Elmore continuous centrifugal has had several notable applications and a uniform discharge with 30 per cent of moisture is obtained. The power required for this operation averages 0.009 kilowatt-hour per pound of moisture-free material.

#### Drying

Drying previous to milling and refining is an important feature of the reclaiming process in its influence upon the characteristics of the final product. Though in the first stages the material may be subjected to somewhat higher temperatures, the final drying temperature should not be over 300° F., and preferably lower. High temperatures will cause depolymerization here also and the invariable result will be a tacky reclaim. If the moisture content is left too high, there is required an excessive milling and refining with a consequent lowering of the desirable qualities. Neither should it be completely dried. A maximum of 8 per cent and a minimum of 5 per cent is ordinarily the preferable range of residual moisture.

In some instances two-stage drying in oil- or gas-fired, direct-heat rotary driers is employed. The flow of material is countercurrent to the hot gases and a comparatively low temperature is maintained in the second stage. In another method the wet material is automatically spread in a thick layer over inclined screens through which heated air is passed. Continuous driers using air heated by steam coils are very efficient and have the advantage of insuring safe and uniform conditions. In this type of drier the initial temperature of the air at the wet end may be as high as 280° F. and the final incoming temperature as low as 150° F.

#### Milling and Refining

Milling and refining are necessary to break up any hard lumps of rubber and to plasticize the reclaimed product to a smooth condition in order to make it suitable for use in rubber compounds. Rubber reclaimed by the direct-steam heater method receives the same general treatment as does alkali reclaim, though usually less milling is required chiefly on account of its low moisture content.

Sixty- or 84-inch standard rubber mills are almost exclusively employed. They are often equipped with aprons which continuously return the material to the bite of the rolls, while in some cases the mills are provided with scrapper devices.

After mastication on mills the material is passed through a rough refiner (or breaker) as many times as are necessary and finally through a finishing refiner. The most modern type of machines has rolls with 30-inch faces, the front roll

being about 24 inches in diameter and the back one 19 inches in diameter. Typical surface speed conditions are about 177 and 70 feet per minute, respectively. The action of this speed differential, combined with the fact that for many materials the rolls of the first refiners are set at about 0.01-inch gage and those of the finishing machines at about 0.005-inch, account for the term applied to the machines and the operation. The output from a finishing refiner will vary from 150 to 500 pounds an hour depending upon the character of the material.

#### Power Required for Milling and Refining

RECLAIM	Kilowatt-hour per lb.
Black tires	0.45
Inner tube	0.265
Solid tire, air-bag, etc.	0.165

It is known that long milling and refining on cold machines greatly increases the plasticity of reclaimed rubber—just as it does raw rubber. It is also true that the qualities of reclaim are unfavorably affected by processing on abnormally hot mills and refiners. Temperatures over 200° F. are dangerous in most cases, grainy reclaim with decreased tensile and elongation resulting from overheating. Mill temperatures of 140° to 160° F. are preferable and the best refining temperature is usually from 165° to 185° F.

The effect of temperatures in milling and refining is illustrated by the accompanying curves. The temperatures indicated are those of the mill and refiner roll surfaces. The reclaim on the mills runs a few degrees hotter than the "working" rolls, but in every case the thin stock from refiners has a temperature very close to that of the front refiner roll.

#### Straining

Straining (followed by sheeting into slabs of convenient size) is ordinarily the final operation and is always necessary in finishing tire reclaim in order to remove small pieces of metal and other foreign matter. Screw-type "strainers" with 26- to 30-mesh screens are used as a rule, though finer screening is practiced in some special cases. There is danger of overheating the reclaim when it is forced through very small openings. Here again temperatures must be controlled in order to preserve the quality of the product.

*Note*—No attempt has been made to discuss the "acid" process, since it is now applied to only a limited class of vulcanized scrap such as rubber footwear with a low sulfur content and to uncured fabric-containing scrap such as tire carcass trimming. However, for similar operations the same factors are at influence as in the alkali and the heater processes.

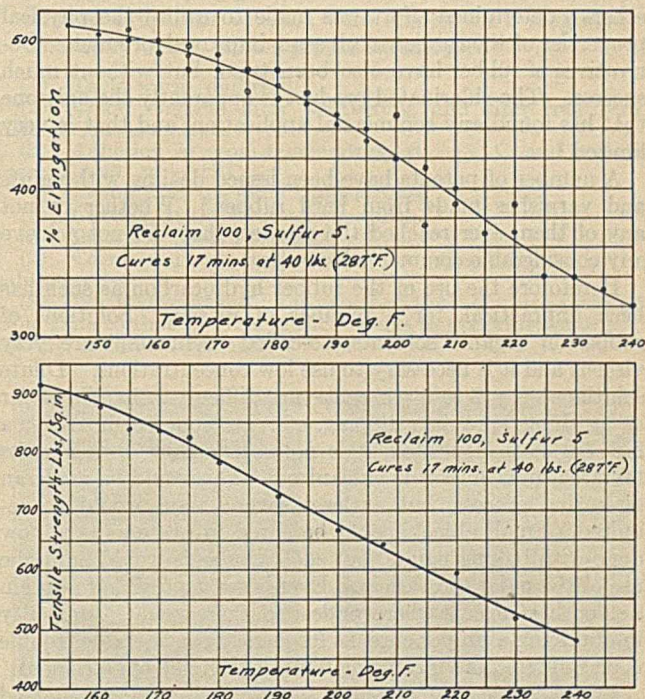
#### Future Developments

The comment is frequently made that there have been no fundamental developments in the art of reclaiming rubber since the basic conceptions of nearly thirty years ago. This is essentially true and improvements in processing have been confined mainly to the adaptation of more efficient manufacturing apparatus. But there has been progress in the raising of quality standards as a result of technical control and a better appreciation of just what characteristics constitute a valuable rubber substitute. The day has just arrived when the research chemist and the engineer have joined forces in a tardy campaign to attempt really to regenerate vulcanized rubber.

Present-day processes never reimpair the two properties of solidity and elasticity exhibited by raw rubber. Vulcanized rubber, especially after long use, has undergone such complex physico-chemical changes that we may never restore it to its original state, though it is certainly not beyond the realm of possibilities in this day of seeming miracles.

Just as vulcanizing is more than the result of the combination of rubber and sulfur, so the removal of the combined sulfur may not be expected to reimpair automatically the properties of the original rubber. When Spence<sup>6</sup> removed a large portion of the combined sulfur from vulcanized rubber with aniline-sodium he obtained a plastic material probably due to the softening effect of the aniline. Dubosc<sup>7</sup> did not obtain a plastic product when he effected the removal of over 50 per cent of the combined sulfur from vulcanized rubber by boiling it in a solution of hexamethylene-tetramine. It seems that in the devulcanizing process we have to deal more with depolymerization or disaggregation; and if the removal of combined sulfur should coincidentally restore vulcanized rubber to something like its original condition, we must look farther than a method such as the alkali process or any of the proposed schemes described in the hundreds of patents on the subject.

Solvent processes cause depolymerization to a high degree, as is shown by the changes in viscosity. The solvent dissolves the depolymerized materials and the product tends to be too soft and tacky for ordinary use. Some modification of Bary's<sup>8</sup> osmotic process in which he employed xylene may be the answer. Catalysis will no doubt play a principal role in true regeneration. The problem merits the attention



Temperature Effect in Milling and Refining Black Tire Reclaim

of the research chemist in coordination with his efforts to learn the mechanism of vulcanization, if for no other reason than that the solution of either may lead to the discovery of the other.

#### Acknowledgment

The writer wishes to express his thanks to J. H. Coultrap, C. H. Smith, and R. W. Moorhouse, of the Goodyear organization, for assistance in preparing this paper, and to the officials of the Philadelphia Rubber Works for information which they kindly gave.

<sup>6</sup> U. S. Patent 1,235,850 (1917).

<sup>7</sup> *Caoutchouc & gutta-percha*, 15, 9440 (1918).

<sup>8</sup> Dubosc and Luttringer, "Rubber, Its Production, Chemistry, and Synthesis," p. 40.

# Protective Paint from Rubber<sup>1</sup>

\*Harold Gray

THE B. F. GOODRICH COMPANY, AKRON, OHIO

**R**UBBER has long been considered for use in the paint industry. Certain of the physical properties of suitably compounded rubber—such as resilience, resistance to shock, low permeability to moisture, high resistance to abrasion, and its characteristic strength—make it a very promising starting material. Several attempts have been made to utilize its unusual properties.

For instance, a small amount of rubber has sometimes been dissolved in the oil in regular lead and oil paints. No doubt in some cases this was for advertising purposes only, but in others a determined effort was made to utilize the physical properties of the rubber to give an improved product. Derivatives of rubber have also been tried, but without much success. The chlorinated product is apparently the only one that has found any commercial application, and that is very limited.<sup>2</sup>

A number of patents have been issued dealing with paints and varnishes made from hard rubber.<sup>3</sup> Whether or not any of them ever reached the market, they did not achieve any considerable commercial success.

Heretofore the use of the rubber hydrocarbon as such has been impractical, for a number of reasons. Solutions of rubber in organic solvents, so-called "cements," are very viscous and it is necessary to use low concentrations. Dilute solutions—say 2 to 5 per cent—are difficult to handle as far as brushing, spraying, dipping, etc., are concerned. After a film has been deposited, it is not satisfactory, owing to its tacky nature, until it is vulcanized. This could be made an air-curing process, but at least several days would be required. Small objects could be cured in heaters, as is now done with baking paints, but such a process would limit the use of the paint too closely. Even were it possible to obtain a smooth, even coat wherever desired, there would be difficulty in obtaining a proper cure, as frequently considerable trouble is encountered in vulcanizing films deposited from a cement.

In the course of an extended series of investigations started by Fisher,<sup>4</sup> there has been perfected in the Goodrich laboratories a technic for modifying the properties of rubber hydrocarbon by means of a change other than vulcanization. A series of products ranging from a tough, horny, balata-like substance to a brittle, pulverizable material resembling shellac is made available by this treatment. The hydrocarbon (which throughout this paper will be designated as "thermoprene") is very pure and has many unusual properties which make it a promising starting material for paints. The outstanding point of interest to the paint chemist is that the concentration of thermoprene in the solvent can be as

A protective paint has been prepared from rubber which can be used commercially. The chief features of the new paint are: (1) good adhesion to metals; (2) resistance to acids, alkalies, corrosive gases, and corrosive chemicals in general; (3) low permeability to moisture, salt solutions, salt spray, etc.; (4) the film is tough and can be bent without injury at sub-zero temperatures; (5) the film does not flake when cut, and rust spreads very slowly from an exposed area.

On account of its unusual set of properties, this paint should have a wide range of usefulness, particularly in chemical and other plants where metal parts are subjected to excessive corrosive conditions.

high as 10 to 20 per cent and still be within the range of good brushing products. The chief difference between thermoprene paint and those previously made with a raw-rubber vehicle is that the former resembles a lacquer in that it needs no vulcanizing or curing operation.

## Properties of Rubber Paint

### RESISTANCE TO CHEMICAL ACTION—

The resistance to acids, alkalies, corrosive gases, and corrosive chemicals in general is very good. Examples are sulfuric acid, sulfur dioxide, sulfur trioxide, hydrochloric acid, hydrogen sulfide, sodium hydroxide, sodium hypochlorite, and calcium hypochlorite.

**RESISTANCE TO MOISTURE PENETRATION—**Low permeability to moisture, desirable in any paint, is shown to a remarkable degree by films of thermoprene. A molded sheet (7 by 7 by  $\frac{1}{20}$  inch or 18 by 18 by 0.13 cm.) gained 0.365 per cent in weight when immersed in water at  $+1^{\circ}$  to  $+2^{\circ}$  C. for 345 days. (Chart 1) Panels covered with the paint and immersed in water show practically none of the discoloration caused by moisture penetration. The importance of this very useful property is shown by the remarkable results obtained with the paint in salt water, salt spray, and under moist conditions in general.

**ADHESION—**Any paint to be of value must adhere firmly to the surface it covers. The high degree of adhesion of the new paint is one of its most important properties. It is practically impossible to separate the film from the underlying surface without actually cutting it. This property is valuable in a number of ways. For example, if a thermo-

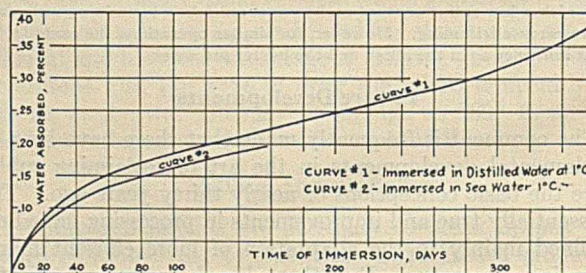


Chart 1—Resistance to Moisture Shown by Rubber Paint

prene film on iron is ruptured, the exposed surface will rust very quickly. The rust, however, will spread very slowly from the exposed area, because the film adheres so firmly to the metal that it will not strip back. When the film is cut with a knife it does not shatter or flake. The cut or scratch is clean and only the portion actually in contact with the cutting device is affected.

**ELASTICITY—**The film is very elastic, as shown by the fact that a piece of steel (4 by 2 by  $\frac{1}{16}$  inch or 10 by 5 by 0.16 cm.) covered with three coats of thermoprene and cooled to  $-18^{\circ}$  to  $-17^{\circ}$  C. can be bent double without injury to the film. A sharp blow with a hammer results in nothing more than

<sup>1</sup> Presented as a part of the Symposium on Lacquers, Surfactors, and Thinners before the Section of Paint and Varnish Chemistry at the 73rd Meeting of the American Chemical Society, Richmond, Va., April 11 to 16, 1927.

<sup>2</sup> Lamble, *Oil Color Trades J.*, **57**, 1250 (1920); *Kolloid-Z.*, **29**, 150 (1921); *Caoutchouc & gutta-percha*, **16**, 9811 (1919).

<sup>3</sup> British Patent 243,966 (1925) on India-rubber varnishes is an example.

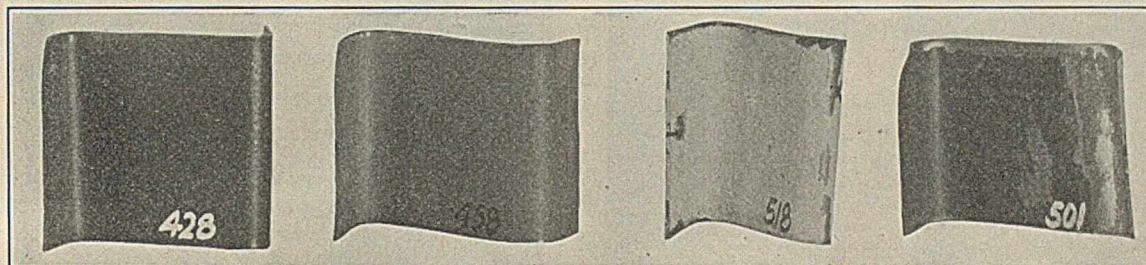
<sup>4</sup> *Ind. Eng. Chem.*, **19**, 1325 (1927).

the cutting of the film at the point of contact. Some of the films were tested at temperatures as low as  $-46^{\circ}$  to  $-51^{\circ}$  C. and showed up as well as at  $0^{\circ}$  C. Cutting the film when cold results in a separation only at the cut portion, with no shattering or flaking.

**RESISTANCE TO TEMPERATURE CHANGES**—Another rather unusual feature of the paint is its resistance to sudden temperature changes. In one series of experiments the films (on steel) were cooled in an ice-salt bath and then put

### Testing Program

In making those tests on composition and general properties, three panels (4 by 12 inches or 10 by 30 cm.) were made in each case, always with three coats and sometimes with four of paint. Of each set, one panel was exposed on the roof on a rack facing south at an angle of 45 degrees from the vertical, one was cut up for laboratory tests, and one was stored for reference.



428—Thermoprene paint      458—Thermoprene paint      518—Commercial lead and oil paint      501—Commercial lacquer  
Plate I—Bending Tests on 2 by 4 by 1/16-Inch (5 by 10 by 0.16-cm.) Steel Panels. One End Bent at  $0^{\circ}$  C. and the Other at Room Temperature

on a hot plate at  $115^{\circ}$  C. After 15 minutes on the hot plate the panels were plunged into the ice water again. This cycle was repeated ten to fifteen times with no apparent effect on the films.

**PIGMENTATION PROPERTIES**—Any desired pigment can be used in the paint and any color except a pure white can be obtained. The amount of pigment can be varied widely. The possible range extends from no pigment at all to as high as 250 or 300 volumes of pigment to 100 volumes of thermoprene. The practical range is yet to be determined. Good results are obtained with 70 volumes of pigment. Color may be imparted by organic dyes, using a white pigment as the filler. A very wide range of oils and softeners can be used. In some cases where a baking paint is desired, drying agents may be used.

**SOLVENT PROPERTIES**—The paint should probably be classed as a lacquer, since a solvent is used which does not remain as a part of the film. In general, the ordinary rubber solvents are used—such as gasoline, toluene, benzene, carbon tetrachloride, turpentine, kerosene, etc. The solvents are varied according to the use for which the paint is intended—i. e., brushing, spraying, or dipping.

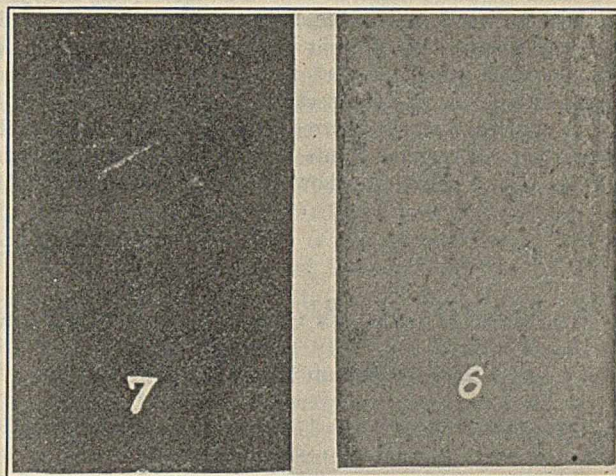
### Laboratory Tests

Comprehensive tests have been conducted to determine the general characteristics of the paint. With respect to composition, the following factors were studied:

- (1) Variations in physical properties of thermoprene.
- (2) Effect of pigments. The more common ones were aluminum, asbestine, barytes, blanc fixe, chromic oxide, clay, gas black, graphite, iron oxide, lead chromate, lithopone, red lead, sienna, Titanox, ultramarine blue, white lead, whiting, zinc oxide, and a series of organic dyes.
- (3) Variations in pigment concentration in under-coat and in top-coat.
- (4) Effect of oils and softeners.
- (5) Effect of driers in the drying oils.
- (6) Time and temperature (compounds used for baking enamels).
- (7) Surface. All the paints were tested on steel. A representative series was also tried on numerous other surfaces including aluminum, brass, and bronze (4 types), copper, Duralumin, iron (4 types), lead, nickel, tin, leaded tin, galvanized iron, zinc, magnesium, red oak, and white pine. Some tests were also made on hard and soft rubber.

General properties of films were studied in a long series of laboratory tests. These properties included:

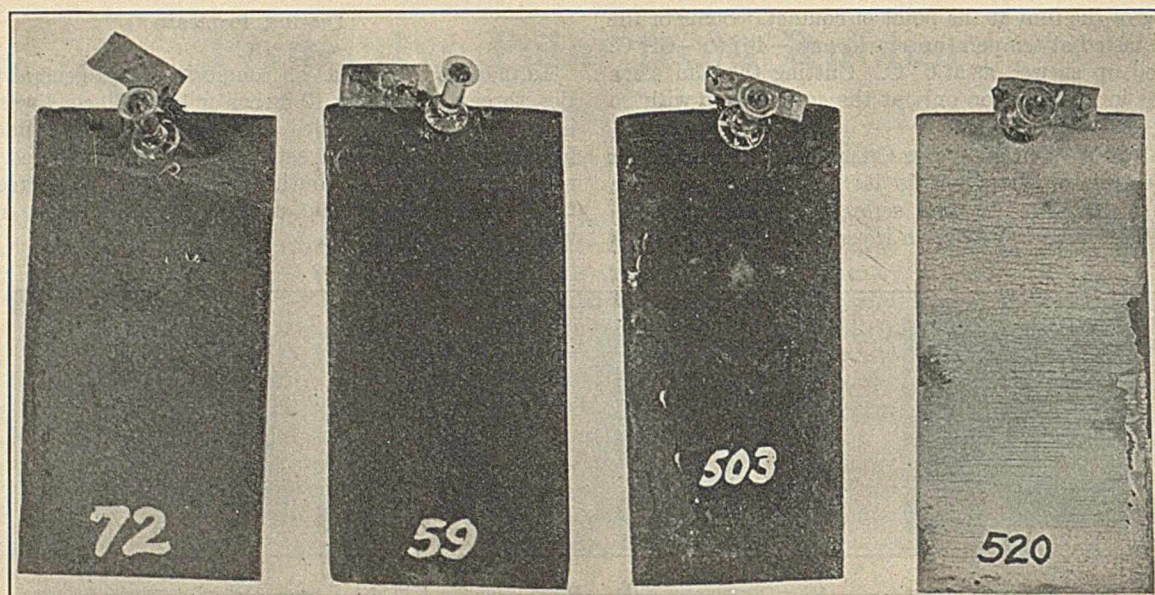
- (1) Tack, warm, and cold.
- (2) Color, original, after weathering, and after treatment with various chemicals.
- (3) Adhesion, at room temperature, at  $-18^{\circ}$  C. and in some cases at  $-46^{\circ}$  to  $-51^{\circ}$  C.
- (4) Bending, at the same temperatures.
- (5) Cutting, at the same temperatures.
- (6) Behavior toward solvents.
- (7) Corrosion resistance toward various chemicals and in the salt-spray test.
- (8) Weather resistance; the panels on the roof were examined from time to time to observe such effects as checking, chalking, rusting, color changes, etc.



7—Lead and oil paint      6—Thermoprene paint  
Plate II—Steel Panels Exposed Five Months in Salt Works

The elaboration of this program of testing required more than two years. At one time there were over twelve hundred weather-exposure panels under observation. The conclusions drawn from this testing program are briefly summarized as follows:

- (1) Physical properties of the thermoprene are uniform, subject to accurate manufacturing control.
- (2) Ordinary paint pigments can be successfully incorporated into these paints over a wide volume range.



72—Thermoprene paint

59—Thermoprene paint

503—Commercial lacquer

520—Commercial lead and oil paint

Plate III—Panels in Salt Spray

(3) Although oils and driers mix well with the paints, there is little advantage to be gained from their use.

(4) As in the case of ordinary paints, baking hardens the film.

(5) Both air-dried and baked films show good adhesion to most metallic and other surfaces. This adhesion persists at temperatures as low as  $-51^{\circ}\text{C}$ .

(6) Direct exposure to weather and sunlight reveals a prevailing tendency toward chalking, occasional checking, and some rusting in spots.

(7) Exposure to acid and alkali and to salt spray indicates that thermoprene has exceptional protective properties.

#### Small-Scale Commercial Tests

The laboratory and roof experiments were supplemented by a series of semicommercial tests tending to show the type of service for which the paint is best adapted. For example, there has always been a great deal of trouble in obtaining a paint which would protect the metal in a salt works. Several test panels and test sections of metal work in such a factory showed that the thermoprene paint stood up much better than commercial paints that had been used before. In Plate II two panels are shown that had been exposed for

five months. Panel 7 was covered with a lead and oil paint, and is completely rusted. There are a few small rust spots on panel 6, which was protected by a thermoprene paint. These rust spots are due to pigment agglomerates, which have now been eliminated by improved methods of manufacture.

The effect of salt spray is further brought out in Plate III. These panels were cut from a 4 by 12 inch (10 by 30 cm.) panel and the edges are raw. The edges were left this way purposely to show how well the films would prevent rust-spreading. There is practically no spread of rust from the edge of the thermoprene paint panels 72 and 59.

In a cooling tower where the spray of steam and cooling water from tire vulcanizers was blown against a series of louvres in a fine spray, at the end of nine months the commercial paints were practically all destroyed, while a few thermoprene paints of a particular composition were in good condition at the end of sixteen months.

These preliminary development tests are now being augmented by painting tests in chemical plants.

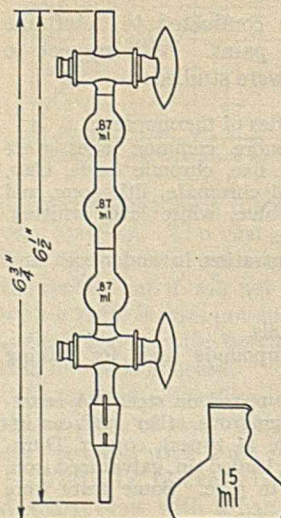
## A Modified Weighing Pipet<sup>1</sup>

Graham Edgar

ETHYL GASOLINE CORPORATION, 25 BROADWAY, NEW YORK, N. Y.

IT IS frequently desirable in analytical work that analyses be made upon a nearly constant quantity of material, and in the case of corrosive liquids or other liquids not readily measurable in ordinary volumetric apparatus, this procedure may be inconvenient. There has been devised in this laboratory a modified Lunge weighing pipet which has proved very useful, and it is described here as being of possible interest to other laboratories where routine analyses are carried out.

The apparatus, illustrated in the accompanying sketch, consists essentially of a Lunge pipet containing three bulbs



of definite volume with graduation marks between them. The base is flattened and is of such dimensions that the pipet will stand comfortably on the ordinary balance pan. By the use of this pipet duplicate or triplicate weighings of nearly the same quantity of material may be conveniently made. The apparatus may be made with two bulbs instead of three and the dimensions of the bulbs may be changed to suit individual needs.

The pipet has been made by the Yonkers Laboratory Supply Co., 549 West 132nd St., New York, N. Y.

<sup>1</sup> Received December 28, 1927.



## CHANDLER LECTURE

In 1910 friends of Professor Chandler presented to the trustees of Columbia University a sum of money which constitutes the Charles Frederick Chandler Foundation. The income from this fund is used to provide a lecture by an eminent chemist and also a medal to be presented to this lecturer in further recognition of his achievements in the chemical field. Under the provisions of this fund the trustees designate from time to time one who has made contributions of notable value and invite him to be the Chandler Lecturer and Medalist.

The award for 1927 was to Dr. Moses Gomberg, chairman of the Department of Chemistry at the University of Michigan, Ann Arbor, Mich., and his lecture was given at Columbia University on the evening of December 16, 1927. In presenting the medal Prof. George B. Pegram referred to the fundamental discoveries of the Medalist as follows:

In his attempt to prepare certain organic compounds, Doctor Gomberg discovered, about 1900, a very interesting chemical behavior of the element carbon. In endeavoring to account for this property, he suggested the idea of trivalent carbon and the

existence of free organic radicals. To the organic chemist, his announcements were revolutionary and served to stimulate research probably more than anything else since Kekulé proposed his atomic linkage idea and benzene theory. The influence of Doctor Gomberg's researches and ideas is now easily recognized in many of our current theories in chemistry.

The previous lecturers, with the titles of their lectures, are as follows:

1914	L. H. Baekeland	Some Aspects of Industrial Chemistry [Vol. 6, 769 (1914)]
1916	W. F. Hillebrand	Our Analytical Chemistry and Its Future [Vol. 9, 170 (1917)]
1920	W. R. Whitney	The Littlest Things in Chemistry [Vol. 12, 599 (1920)]
1921	F. G. Hopkins	Newer Aspects of the Nutrition Problem [Vol. 14, 64 (1922)]
1922	E. F. Smith	Samuel Latham Mitchell—A Father in American Chemistry [Vol. 14, 556 (1922)]
1923	R. E. Swain	Atmospheric Pollution by Industrial Wastes [Vol. 15, 296 (1923)]
1925	E. C. Kendall	Influence of the Thyroid Gland on Oxidation in the Animal Organism [Vol. 17, 525 (1925)]
1926	S. W. Parr	The Constitution of Coal—Having Special Reference to the Problems of Carbonization [Vol. 18, 640 (1926)]

## Radicals in Chemistry, Past and Present

Moses Gomberg

UNIVERSITY OF MICHIGAN, ANN ARBOR, MICH.

THE conditions that go with the nomination of the speaker for this happy occasion extend to him the privilege, and in a measure make it incumbent upon him, to present a brief account of his own contribution in some branch of chemistry. An attempt to give such an account in this instance is not without difficulties, largely because of the specialized nature of the topic to be discussed. None the less, a brief survey of the history of free radicals will be given, with the emphasis mainly on those aspects which may not be devoid of general interest.

### RADICALS 1815-58<sup>1</sup>

#### Lavoisier's Radicals (1785-1815)

The term "radical" we owe to Lavoisier. In accordance with his conception of the supreme role played by oxygen, to Lavoisier the great majority of the mineral substances were oxygen compounds, the bases being oxidized metals, the acids oxidized non-metals, and the salts combinations of these two. The fundamental stuff which through its oxidation gives rise to base or acid Lavoisier designated as the "radical." At that time (1785) about twenty-five of these radicals—elements as we call them now—were known to be capable of existence in the free state. Lavoisier, however, had no doubt that in time still other such radicals would be isolated from their acid or base combinations.

We owe to Lavoisier also the first methods of determining the composition of so-called organic compounds. He analyzed alcohol, olive oil, tallow, fruit acids, etc., and his conclusion was this:

<sup>1</sup> The writer feels particularly indebted to Lowry's "Historical Introduction to Chemistry," Macmillan and Co. (1915); Hjelt's "Geschichte der organischen Chemie," Vieweg und Sohn (1916); Graebe's "Geschichte der organischen Chemie," J. Springer (1920); Lipmann's "Zeittafeln zur Geschichte der organischen Chemie," J. Springer (1921).

I have observed that in the mineral kingdom almost all oxidizable radicals were *simple*; that in the vegetable kingdom, on the contrary, and above all in the animal kingdom, there were scarcely any which were composed of less than two substances, hydrogen and carbon; that often nitrogen and phosphorus were also present; in this manner radicals were produced consisting of four components.

Very little progress was made during the next fifteen years. Nor did the first decade of the nineteenth century bring any important advance in the field of organic chemistry, rich as that decade proved for inorganic chemistry: Berthollet's "Essai de statique chimique" (1803), Proust's Law of Constant Proportions (1801-8), Dalton's Law of Multiple Proportions and the beginnings of his Atomic Theory (1804), the electrolytic separation of the alkali metals by Davy (1807), Gay-Lussac's Law of Combining Volumes (1808), Berzelius' first paper on the "Constancy of Composition in the Inorganic Compounds (1810), and finally Avogadro's Hypothesis (1811). The principal reason why organic chemistry remained nearly stationary for the twenty-five years following the work of Lavoisier was that no satisfactory and ready method for the quantitative analysis of organic substances was known. There was no way of testing old or new theories. This became possible only after Gay-Lussac and Thenard, in 1810, presented a fairly accurate method of determining quantitatively the composition of organic substances. Berzelius soon introduced further important improvements, so that in 1813, with his wonderful skill in analyzing, he could make an analysis in three months and was able to carry through in one year the analysis of as many as fourteen substances.

### The Cyanogen Radical

The new methods of analysis soon began to yield fruit. The year 1815 marks indeed a milestone in the history of

organic chemistry. Gay-Lussac prepared for the first time anhydrous, pure prussic acid, and determined its composition as HCN. He made from the acid a number of salts and other derivatives and found that all of them retained the part (CN) originally present in the acid. Said Gay-Lussac:

There is, then, a very great analogy between prussic acid and hydrochloric and hydriodic acid: like them, it has a radical which combines with potassium, and forms a compound quite analogous with chloride and iodide of potassium: only this radical is *compound*, where chlorine and iodine are *simple*.

Gay-Lussac designated the radical of prussic acid as "cyanogen," and finally he succeeded in obtaining the cyanogen gas itself in the free, uncombined state. For the first time a compound radical had been isolated as such. Lavoisier's prophecy had been vindicated, and his early generalizations could now be reaffirmed with greater force. Said Berzelius in 1817:

In inorganic nature all oxidized bodies contain a *simple radical*, while all organic substances are oxides of *compound radicals*. The radicals of vegetable substances consist generally of carbon and hydrogen, and those of animal substances of carbon, hydrogen and nitrogen.

Henceforth this dualistic theory of organic matter—i. e., radical plus oxygen—persisted in its various guises for almost fifty years, and the theory of compound radicals played in one form or another a dominant part in the development of organic chemistry. Are all the vegetable acids derived from one and the same compound radical? If not, how many different such radicals are there? What is the radical of the carbohydrates, of fats? What is the exact composition of each individual radical? May not the molecule contain several radicals, all equally important? Does the radical really represent a compact cluster which is as immutable and as indivisible as are the elementary atoms in the mineral kingdom? Or are these radicals themselves subject to change? If changeable, why consider them as of greater importance in the molecule than the other components?

One after another these questions came to the fore, and the answer to each brought with it a slightly different hypothesis in regard to the constitution of organic molecules.

#### The Etherin Theory (1827-37)

As far back as 1815 Gay-Lussac, on the basis of the respective vapor densities of alcohol and ether, arrived at the conclusion that alcohol might be a combination of one volume of ethylene with one of water, and ether of two volumes ethylene with one of water. About a dozen years later Dumas and Boullay determined carefully the composition of alcohol and of ether, and they confirmed the conclusions of Gay-Lussac. Dumas and Boullay also determined the composition of various organic esters of alcohol, and made the sweeping suggestion that alcohol, ether, and their esters could all be considered as derivatives of ethylene. In justification of their view they pointed to these facts: (1) ethylene is actually obtainable from alcohol; (2) ethylene combines with sulfuric acid, and from this combination alcohol or ether can be regenerated, as had been shown by Faraday and Hennel. The evidence seemed complete that ethylene was the compound radical which preëxisted in all these substances:

SUBSTANCE	MODERN FORMULA	DUMAS' FORMULA
Ethylene	$C_2H_4$	$C_2H_4$ (etherin)
Alcohol	$C_2H_6O$	$C_2H_4 \cdot H_2O$
Ether	$(C_2H_5)_2O$	$C_2H_4 \cdot \frac{1}{2}H_2O$
Ethyl chloride	$C_2H_5Cl$	$C_2H_4 \cdot HCl$
Ethyl acetate	$C_2H_5 \cdot C_2H_3O_2$	$C_2H_4 \cdot C_2H_3O_2$

The etherin thus constitutes historically the second compound radical for the independent existence of which claim was being made. Later the etherin theory was extended to

methyl alcohol and to other alcohols as well. For the first time it became possible to classify systematically organic compounds into groups, each group around one common radical—ethylene, methylene, etc. At first Berzelius accepted the etherin theory, but later he began to doubt the validity of this view, because Dumas' formulas for the derivatives of etherin did not appear to Berzelius, nor to Liebig, to harmonize with their behavior. If alcohol and ether were really hydrates, then calcium oxide should convert them into ethylene—and yet it did not. The etherin theory, none the less, held sway for ten years, when Dumas finally conceded that ethyl, rather than ethylene, was likely to be the true compound radical. Thus etherin, as a radical with independent existence, disappears from the stage, giving place to the hypothetical ethyl of Berzelius and Liebig.

#### Benzoyl Radical

Of unusually great influence proved to be the classic investigation of Wöhler and Liebig on the benzoic acid radical. This extensive study was commenced in the middle of May, 1832, and was completed in August of the same year. Starting with oil of bitter almonds, our benzaldehyde, they found that they could convert it successively into a series of related compounds, in all of which the group ( $C_7H_5O$ ) remained unaltered:

Oil of bitter almonds	$C_7H_5O \cdot H$
Benzoyl chloride	$C_7H_5O \cdot Cl$
Benzoyl cyanide	$C_7H_5O \cdot CN$
Benzoic acid	$C_7H_5O \cdot OH$
Benzamide	$C_7H_5O \cdot NH_2$
(Benzoyl)	( $C_7H_5O$ )

To quote from them:

Organic substances may be arranged around a common center, a group of atoms preserving intact its nature and composition amid the most varied associations with other components. This stability, this analogy, justifies one to regard this group as equivalent to an element, as a kind of a compound element; we propose for this radical the special name Benzoyl.

Wöhler and Liebig's investigation, and its exceptionally favorable reception by Berzelius, produced a strong impression, notwithstanding the fact that the benzoyl radical itself seemed to elude isolation in the free state. Within two years after the publication of this famous investigation, there appeared a paper by Aug. Laurent,<sup>2</sup> in which the claim was made, with some slight reservations, that the very benzoyl radical itself was prepared by him. What an ironical incident! Laurent, who was destined to become in later years one of the bitterest opponents of the radical theory, should at this time, 1835, seem to be supplying Wöhler and Liebig with the very cornerstone of their benzoyl theory. More curious still is the fact that Liebig should be producing seemingly effective experimental evidence that Laurent's benzoyl has no connection with the true surmised radical of the benzoyl series.<sup>3</sup> And yet, from our present point of view, Laurent's substance was fully as much entitled to be classed among the radicals as any of the other compounds which, in subsequent years, were designated as free radicals, as it really was dibenzoyl ( $C_6H_5CO$ )<sub>2</sub>.

The scheme proposed by Wöhler and Liebig of grouping a number of related substances around the benzoyl radical was soon extended by other investigators to other compounds. Piria, in Pisa, applied the theory to the salicylic acid group with its corresponding salicyl radical.

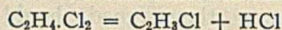
#### Radicals Are Not Immutable

It was becoming evident at this period that the groups which had been assumed to be the compound radicals were

<sup>2</sup> *Ann. chim.*, 59, 397 (1835).

<sup>3</sup> Hofmann, "The Life-Work of Liebig," Macmillan and Co., p. 82 (1876).

themselves not at all immune against change in composition when subjected to the influence of certain reagents. As argument against the immutability of radicals can be cited Regnault's investigation, which was carried out, strangely enough, in Liebig's own laboratory (1834-5). According to the etherin theory, ethylene dichloride was one of the most typical etherin compounds ( $C_2H_4 + Cl_2$ ). Regnault found, however, that this substance, when heated with alcoholic potash, broke up into two substances as follows:



Obviously, the two chlorine atoms in the original compound played different functions—one atom being removable, the other not; consequently, not ( $C_2H_4 + Cl_2$ ) is the make-up of the molecule, but ( $C_2H_3Cl + HCl$ ). One of the two inevitable conclusions must now be drawn: either the compound radical ( $C_2H_4$ ) is not immutable, or not ( $C_2H_4$ ), but ( $C_2H_3$ ), is the true radical. The defenders of the radical theory promptly adopted the second alternative. Liebig thought that this conclusion disposed once and for all of Dumas' etherin radical. He was right in that, but the conclusion worked equal havoc with his own ethyl radical—neither ( $C_2H_4$ ) nor ( $C_2H_5$ ) could now be considered as the unchangeable compound radical. Indeed, fifteen years previously Faraday obtained by the action of chlorine gas on  $C_2H_4Cl_2$  the compound  $C_2Cl_6$ ; consequently the group ( $C_2H_3$ ), in its turn, cannot be considered the true radical. Then came the crucial experiments of Dumas and of Laurent, which finally culminated, by 1840, in their well-known Theory of Substitution: Any hydrogen in the molecule, be it a part of the surmised radical or not, is equally subject to substitution by halogen, without very material change in the properties of the substance itself; for instance, compare acetic with trichloroacetic acid. The inference came about naturally that, not the composition of the radical in the molecule, but rather the type of the structure of the whole molecule was the responsible factor of the properties of the substance.

At first Liebig, as well as Berzelius, strenuously opposed the notion that radicals are subject to change. Moreover, as a follower of Lavoisier, Berzelius consistently rejected the inclusion of the electronegative oxygen or chlorine as an integral part of the radicals, and he was thus led to devise, with frequent revisions, new radicals for various substituted halogen compounds; for instance, benzaldehyde, previously considered as  $(C_7H_5O).H$ , became now  $(C_7H_5).O$ ; tetrachloroether ( $C_4H_6Cl_4O$ ) became a conjugated compound ( $C_2H_6O + C_2Cl_4$ ). Liebig, on the other hand, saw the advantages of the substitution theory, but he still favored the theory of radicals in its general features for purposes of classification.

#### Do Radicals Have an Objective Reality? (1834-42)

Still another factor militated seriously against the theory of radicals. In 1834, in discussing the relation of ethylene, alcohol, and ethyl ether, Liebig used these words: "I doubt not that the radical of ether, namely, the hydrocarbon Ethyl, will be isolated in the free state." Several years later, however, the existence of ethyl as well as of other radicals was still only a matter of faith and of hope, Gay-Lussac's cyano-

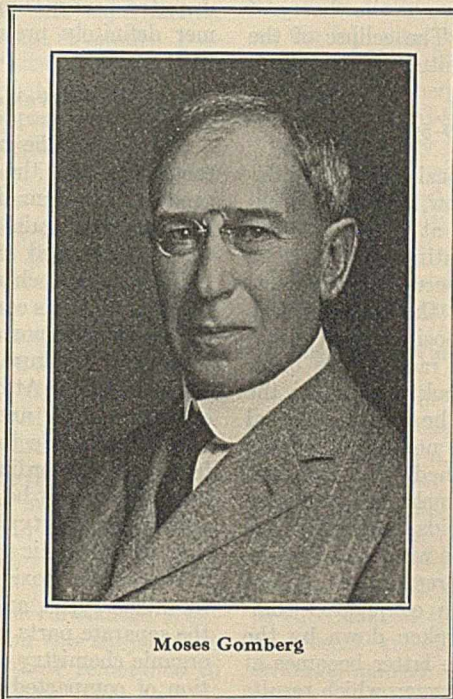
gen and Dumas' doubtful etherin being the only two examples. Said Liebig in 1838:

The organic radicals are known to us for the most part merely as hypothetical substances, but as regards their actual existence, there can be no more doubt than there is any doubt in regard to the existence of the inorganic radical of nitric acid ( $N_2O_3$ ), although this, like ethyl, is as yet unknown.

It makes rather strange reading to find that Dumas, under the persuasive powers of Liebig, threw at this time (1837) his influence on the side of the radical theory, for a while at least. Jointly the two addressed to the Paris Academy a note entitled, "The Present State of Organic Chemistry." They made a passionate appeal in behalf of the radical theory, which they called the "natural classification of organic compounds."

Organic chemistry possesses its own elements, some of which play a role similar to that of chlorine or oxygen in inorganic chemistry, and some play the role of metals.—Cyanogen, Amido, Benzoyl, are the very elements of which organic chemistry makes use in its operations.

Rhetoric alone was, however, not sufficient to counteract the influence of newer theories, based as these were upon the experimental evidence of substitution. If organic chemistry was to be defined with Liebig as the chemistry of radicals, "then," in the words of Gerhardt, himself a former pupil of Liebig, "it is the Chemistry of the Things Non-existent." Another powerful opponent, a former pupil of Dumas, challenged (1840) Berzelius to produce for him a single free radical; then he, Laurent, would concede on grounds of analogy the existence of all other presumptive radicals. Alas, proponents of the theory had no reply to make to this challenge, and the



Moses Gomberg

theory of radicals might not have been carried over into the fifth decade of the century were it not for the timely appearance of the classic investigations by Bunsen, from the period 1837-42.

#### The Cacodyl Radical

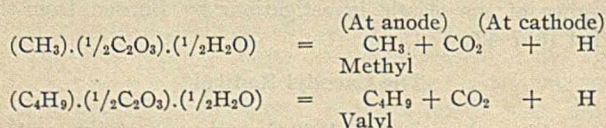
It had been known since 1760 that when potassium acetate and white arsenic are heated together a fuming offensive smelling substance is produced which is very poisonous and which inflames spontaneously on exposure to air. Bunsen, just starting on his scientific career, made a complete analysis of this so-called "Cadet's fuming liquid." By fractional distillation he separated from it a substance the composition of which he proved to be  $((C_2H_6)As)_2O$ , for which Berzelius suggested the name "cacodyl oxide." From this oxide a whole series of derivatives was prepared—the chloride, bromide, cyanide, sulfide, etc.—and they all retained the complex  $(C_2H_6)As$  unchanged. The original oxide behaved thus like a metallic oxide, with the complex  $(C_2H_6)As$  corresponding to the metal. Finally, by treating the cacodyl chloride with zinc, the cacodyl itself was liberated as such. The independent existence of a ternary complex, possessing all the attributes of a metal, was thus no longer fiction. This complex was, in the words of Bunsen, "a true organic element." It is not difficult to comprehend how elated Berzelius was at this discovery. Here at last, coming twenty-five years after cyanogen, was an example of the reality of compound radicals. "This dis-

covery is truly a *curus triumphalis* which will march right through, and will completely smash, Dumas' barricades of bizarre speculations."

Alas, magnificent as was Bunsen's contribution, it could not, standing as an isolated example of free radicals, stem the rising tide of objections to the artificial system of radicals. About this time Liebig was beginning to withdraw from theoretical organic chemistry into agricultural and physiological branches. Berzelius himself was now recognizing clearly the importance of the substitution theories, but in order to uphold at all costs his dualistic system of matter, he was becoming more and more involved in inventing new and strange formulas. Dumas, Laurent, and particularly Gerhard were pushing their new theories through various modifications, which became known as the theory of nuclei, or of residues, or of types, etc. The eclipse of the radical theory seemed imminent, but the situation was saved once more.

#### The Alcohol Radicals (1849-50)

Bunsen had obtained the cacodyl radical from its chloride by heating the latter with zinc; so now, in 1848, Frankland and Kolbe, in Bunsen's laboratory at Marburg, were trying to obtain the ethyl radical by treating ethyl cyanide with metallic potassium. A reaction did occur, but the result was not the one anticipated: instead of the radical ethyl, they obtained a gas which had the composition  $(CH_3)$ , and which they considered to be the methyl radical. In order to verify this conclusion, Kolbe undertook to prepare the same methyl by what seemed to him to be a more rational method, by a reaction which would leave no doubt that the methyl radical was actually the one formed. He thus embarked upon his historic experiment—namely, the electrolysis of the potassium salts of the fatty acids. Although the reaction proceeded not quite in accordance with his premises, he found no difficulty in explaining the reaction as it does occur: Acetic acid, considered by him a conjugated compound of methyl with oxalic acid, is broken down by the current into methyl and oxalic acid; the latter becomes at once oxidized to carbon dioxide by the oxygen which results from the simultaneous electrolysis of the water while the hydrogen of the water goes to the cathode. Electrolysis of valeric acid yields similarly the valyl radical.



Frankland proceeded in a different manner. At the time of his cacodyl experiments Bunsen, in the hope of obtaining also free alkyl radicals, heated to their respective boiling temperatures various alkyl chlorides with metals. No reaction occurred. "It would," he remarked, "prove of great interest to heat under pressure of their own vapors the various organic chlorides with metals." That is exactly what Frankland undertook to do. Introducing for the first time in the history of chemistry the use of ethyl iodide as a reagent, in preference to the chloride or bromide, Frankland heated under pressure in sealed tubes the iodide with metallic zinc as high as 150° C. On opening the tube he obtained, as one of the several products, a gas of the composition  $(C_2H_5)$ . He took it to be the free radical ethyl. Similar experiments with methyl iodide and amyl iodide gave corresponding results—the methyl radical and the amyl radical. Summing up, in 1850, his own and Kolbe's results, Frankland concluded: "The isolation of these four compound radicals (methyl, ethyl, valyl, and amyl)—disposes of all doubt as to their actual existence." This conclusion was at once chal-

lenged by Gerhardt, by Laurent, by A. W. Hoffmann. They insisted that the substances described should each have their formulas doubled, that they represented in each case, not free radicals, but radical in combination with a similar radical; methyl, for instance, was in reality dimethyl,  $(CH_3)(CH_3)$ . Kolbe and Frankland took refuge in the reply that, even if so, dimethyl was not necessarily ethane; the former was  $(CH_3)_2$ , and was a compound radical, while the true ethane was a hydride of the ethyl radical  $(C_2H_5)H$ . These two substances, they argued, should not be identical, but merely isomeric, and their own results indicated, in fact, a distinct difference in properties between their dimethyl and ethane. This conclusion was not accepted by many chemists of that time. Nevertheless it remained in the literature undisputed by experimental evidence till 1864, when Schorlemmer definitely proved the identity of dimethyl and ethyl hydride.

#### Advent of Valence Theory—Structural Chemistry

Thus, with the opening of the second half of the nineteenth century, the theory of radicals as a basis for a comprehensive system of classification received a further reprieve, because once again the actual existence of radicals appeared to be supported by experiment. Meanwhile the whole philosophy of chemistry was undergoing rapid change. Whether radicals can or cannot exist was becoming a question of secondary importance. Not the composition of the radical but the architecture of the molecule became the all-important consideration. At first only two types of architecture were suggested, their number then increased to four, and the attempt was made to classify all known compounds into the few groups according to the surmised type of their architecture: whether it be that of  $H_2$ ,  $H_2O$ ,  $NH_3$ ,  $CH_4$ . (Not to be outdone by the typists, Kolbe proposed his own, and showed that most organic compounds could be considered as derived from carbon dioxide.) Simple types became supplemented by mixed types, and finally the valence theory cemented all the separate parts of truth into one whole. Our present-day organic chemistry came into being. Not the probable function of compacted groups of atoms, not that of radicals, be they real or imaginary, but the function of every individual atom in the molecule—this became the paramount question in chemistry. How well this question has been answered, we all know. The whole dispute as to whether organic radicals can or cannot exist lost completely its original significance. If, as had been postulated by Kekulé, carbon must always function as quadrivalent, then free radicals cannot possibly exist, for they imply bi- or tri-valence of some carbon atom in the molecule. What, then, becomes of those free radicals that have been isolated in the first half of the nineteenth century? A reinvestigation in the light of the new valence hypothesis, supplemented, at this time at the insistence of Cannizzaro, by the forgotten Avogadro hypothesis, discloses the fact that none of these were in reality free radicals. In the light of reinvestigation they now become saturated molecules, the molecular formulas becoming doubled in each case, leaving no carbon atom in the trivalent state. There are no free radicals.

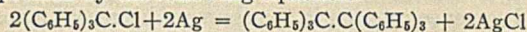
#### RADICALS (1900—)

##### Triarylmethyls

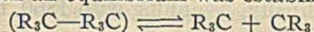
For full forty-two years, from 1858 till 1900, the valence hypothesis continued to serve as the one reliable guide in the phenomenal development of organic chemistry. Several successive generations of chemists were brought up with it, and the quadrivalent nature of carbon, the constancy of quadrivalence, served as the cornerstone of this whole development. One by one countless numbers of compounds

were assigned a definite constitution or a "structure," to use the happy words of Butlerow (1861).

It was against this background of uninterrupted progress for almost half a century that a publication appeared with the startling title, "Triphenylmethyl, an Instance of Trivalent Carbon."<sup>4</sup> The original intention of the experimenter was to prepare a new substance of the composition  $(C_6H_5)_3C_2$ , —i. e., hexaphenylethane. The experiment was carried out in strictly orthodox manner, in conformity with well-tried and well-established procedure. The anticipated reaction may be expressed by the following equation:



Moreover, in view of the presumptive structure of the new compound, one was justified in predicting the properties that might characterize it. The surprise of the experimenter may well be imagined when the resulting substance possessed not one of the surmised characteristics. Instead of being colorless, it proved to be deeply colored; instead of being stable and inert, it was the very opposite—it instantly combined with the oxygen of the atmosphere. Instead of being unresponsive to the action of iodine, it greedily united with it. It was affected by merest traces of acids; decomposed by light. Instead of being non-electrolytic, it conducted the electric current. In brief, it showed characteristics which singled it out from all known classes of organic compounds. In order to account for this unusual behavior, the plausible hypothesis was finally formulated that the two groups,  $(C_6H_5)_3C$ , failed to unite with each other, or, if union had occurred, then spontaneous reverse dissociation was also taking place until an equilibrium was established:



In terms of the old chemistry, we had here free radicals of the order of the methyl; in terms of the modern structural chemistry, it meant that the substance had one carbon atom which functioned, not in the quadrivalent state, but only as trivalent.

It was quite natural that, in spite of the substantial arguments advanced in the first publication on this subject, the chemical profession as a whole should show reluctance to accept the views advanced. Suggestions came from various sources, how one might perhaps explain the properties of the new substance still in terms of quadrivalence instead of trivalence of carbon. Objections so raised were answered by new and more decisive experiments. After ten years of work in several laboratories in this country and abroad (Chichibabin, Schmidlin, Wieland, Schlenk), all obstacles were swept aside and the doctrine of the constant quadrivalence of carbon was dethroned. By 1910 it became universally recognized that the isolation of free radicals was an accomplished fact. In the course of this long controversy it became necessary to prepare other free radicals, and to study these in detail. At the present time there are known to exist over one hundred substances, each indisputably with a carbon atom in the trivalent state. Trivalency of carbon is no longer anomalous; it is encountered infrequently because the substances of this type are too reactive to persist under our every-day methods of experimentation, and they undergo rapid change into more stable systems.

#### Stability and Constitution

It has been mentioned above that whenever we speak of free radicals we really have in mind the system indicating equilibrium between free radical and its demolecular normal ethane compound. What are the factors that impart stability to the free radicals, or, in other words, what are the factors that favor dissociation of the ethane molecule into free radicals? In common with all other instances of disso-

ciation, increase of dilution or elevation of the temperature augments the amount of dissociation of the ethane into free radicals. But of far greater importance is the nature of the three groups which are linked to the central carbon atoms. So slight a change as the substitution of  $(C_6H_5)_3$  by the group  $(CH_3OC_6H_4)_3$  increases the dissociation from 5 per cent to 100 per cent.<sup>5</sup> There are other groups which exert a similar influence, such as naphthyl, biphenyl, etc. Nor is it essential that all three groups linked to the carbon atom be aromatic groups. Through the work of Ziegler, of Conant, of Dufraise, of Schlenk, and of others, we have become familiar with enough instances where one of the three groups may be aliphatic, and still there is dissociation into free radicals. Moreover, at least one of the three groups may be linked to the central carbon atom through oxygen instead of carbon, as the following examples illustrate ( $R$  = aromatic group):  $R_2C-O-C_6H_5$  (Wieland),  $R_2C-ONa$  (Schlenk),  $R_2C-O-MgI$  (Gomberg and Bachmann).<sup>6</sup> The last two classes, known as metal-ketyls, constitute a very large group, as practically every aromatic ketone is capable of such derivatives. It may also be added that individual compounds have been recently described which are assumed to contain, simultaneously, in one and the same molecule, two carbon atoms each in the trivalent state.<sup>7</sup> One wonders—will this view be ultimately extended to our well-known ethylene compounds, to the benzene molecule?

#### Anomalous Valence in Elements Other than Carbon<sup>8</sup>

After it had been definitely established that our orthodox conception of valence constancy of carbon had been erroneous, a skeptical attitude was engendered in regard to other elements. It has, in fact, proved possible to prepare radicals wherein elements other than carbon function in anomalous state of valence. In nearly all cases, tin excepting, the element under investigation was loaded to its limit with phenyl or other aromatic groups, since that configuration had proved so successful in the case of the carbon atom. Radicals are at present known with nitrogen bivalent (Wieland, Goldschmidt) instead of the usual trivalent; with sulfur (Lecher) or oxygen (Pummerer, Goldschmidt) as univalent; tin trivalent (Rugheimer, Kraus), and lead as trivalent (Krause); with silicon also presumably trivalent; only recently radicals were described with boron as quadrivalent,<sup>9</sup> and with chromium as quadrivalent and univalent.<sup>10</sup> Again, if results obtained recently in our laboratory (Gomberg and Bachmann) will be confirmed by further work, we shall be in a position to add to that list examples wherein magnesium functions as a univalent element. Using entirely distinct methods, Manchot and his co-workers quite recently found that still other metals possess a latent tendency towards anomalous valence; he speaks of univalent cobalt, nickel, iron, manganese.<sup>11</sup> Barbieri<sup>12</sup> describes compounds of trivalent manganese and of divalent silver. We may also mention the attempts to isolate free acid radicals:  $CNS^{13a}$  and  $ClO_4^{13b}$ .

Time does not permit more than mere mention of the striking spectroscopic evidence in regard to the variability

<sup>5</sup> Lund, *J. Am. Chem. Soc.*, **49**, 1349 (1927).

<sup>6</sup> *Ibid.*, **49**, 236, 2584 (1927).

<sup>7</sup> *Ibid.*, p. 247; Ingold and Marshall, *J. Chem. Soc. (London)*, **129**, 3080 (1926); Scholl, *Ber.*, **60**, 1236 (1927).

<sup>8</sup> Reviews, with references to literature: (a) Schmidlin, "Triphenylmethyl," Enke (1914); (b) Walden, "Chemie der freien Radicale," Hirzel (1924); (c) Gomberg, *Chem. Rev.*, **1**, 91 (1924); (d) Stewart, "Recent Advances in Organic Chemistry," Vol. II, p. 277, Longmans, Green and Co., 1925.

<sup>9</sup> Wahl, *Z. anorg. allgem. Chem.*, **32**, 157 (1926).

<sup>10</sup> Hein and Eissner, *Ber.*, **59**, 362 (1926).

<sup>11</sup> Manchot and Gall, *Ibid.*, **60**, 191, 2175, 2318 (1927).

<sup>12</sup> *Ber.*, **60**, 2421, 2424 (1927).

<sup>13</sup> (a) Soderbäck, *Ann.*, **419**, 219 (1919); (b) Gomberg, *J. Am. Chem. Soc.*, **45**, 398 (1923).

<sup>4</sup> Gomberg, *J. Am. Chem. Soc.*, **22**, 757 (1900).

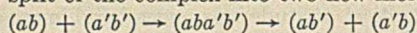
of valence in metals. In the production of their spark spectra, atoms of multivalent metals seem to become stripped of their valence electrons, one by one, giving rise to ion-atom of most varied anomalous valence, such as univalent magnesium, calcium, strontium; univalent and bivalent aluminum, etc. (Fowler; Saunders and Russell). Moreover, there is spectroscopic evidence for the formation of electrically neutral molecules of the type  $\text{CaCl}$ , when the halide salts of the alkaline-earth metals are fed into a Bunsen flame (Mulliken).

The question arises—shall the name "radical" be applied to every newly discovered compound in which some element functions in a state of valence hitherto considered anomalous for it? Yes and no; it is wholly a matter of definition. ( $\text{MgI}$ ) is as much a radical in its relation to  $\text{MgI}_2$  as  $(\text{C}_6\text{H}_5)_3\text{C}$  is in relation to  $(\text{C}_6\text{H}_5)_3\text{C.I.}$  Both are "odd molecules," in the language of G. N. Lewis; each contains an unshared valence electron.

### Explaining Mechanism of Reactions

In the study of phenomena three questions present themselves in succession. What happens? How does it happen? Why does it happen? In organic chemistry we know the answer to the first question in a number of cases; but our replies to the second are by no means plentiful.<sup>14</sup>

It seems, here is where the new knowledge in regard to anomalous valence may prove of service. Kekulé, in his pardonable aversion toward all and any radicals, sought to explain the mechanism of chemical reactions by assuming that there is first addition of the reactants to each other, with subsequent split of the complex into two new molecules:

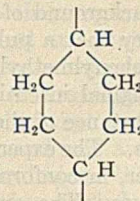


It is, however, evidently becoming more and more customary to interpret the mechanism of many reactions by assuming that the reacting molecules first split into respective radicals, and these then unite to form new molecules. Levine<sup>15</sup> attempts to interpret in this manner the fermentation of glucose. He attributes to the yeast cell the ability to discriminate between glucose passive and glucose active. The

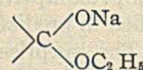
<sup>14</sup> Stewart, "Recent Advances in Organic Chemistry," Vol. II, p. 363.

<sup>15</sup> Science, 66, 560 (1927).

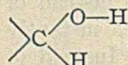
active glucose is a free radical, and so falls victim to the yeast cell. Zelinski<sup>16</sup> blames the hexane compound,



with its two trivalent carbon atoms, for the terrific explosions he has been encountering in the course of his recent investigation. Scheibler<sup>17</sup> claims to have isolated the bivalent radical



and he attributes the formation of methanol from carbon monoxide to intermediate formation of the divalent radical



These are but a few illustrations of the many from the literature of the last few months.

### Conclusion

In the evolution of our organic chemical theories for 1800–1860, there was the ever-recurring refrain: Are there radicals; do they have an independent existence? The existence of radicals—i. e., of part-molecules in distinct contrast to whole molecules—has been, in turn, surmised, believed in, considered as demonstrated; then the question became debatable; and finally, beginning with 1860, the independent existence of radicals was looked upon as wholly improbable. After a lapse of half a century the interest in the subject was revived, and the historic quest for the free radicals has been brought to a successful issue. Hitherto, the definitely recognized units in chemistry have been: atoms, molecules, ions, and electrons. And now, in addition to these four, chemistry, it seems, has to take into account a fifth entity—free radicals.

<sup>16</sup> Ber., 60, 1107 (1927).

<sup>17</sup> Z. angew. Chem., 40, 1072 (1927).

## Distribution of Sulfur in Oil Shale—II<sup>1</sup>

E. P. Harding and Walter H. Dumke

UNIVERSITY OF MINNESOTA, MINNEAPOLIS, MINN.

THIS paper is a continuation of another paper under the same title,<sup>2</sup> and the same methods of analyses were used.

Two oil shales were investigated—an Elko Nevada shale used by the Catlin Shale Products Company and a shale from the Green River formation in Utah. The following results were obtained:

	ELKO NEVADA	GREEN RIVER, UTAH
	Per cent	Per cent
Total sulfur	4.946	1.101
Sulfide and sulfate sulfur	3.998	0.556
Sulfate sulfur	0.406	0.146
Sulfide sulfur	3.592	0.410
Organic sulfur	0.948	0.545
Humus sulfur	0.948	0.540
Resinic sulfur	0.000	0.005

A Mount Logan shale from the Green River formation in Colorado, used by the Mount Logan Oil Shale Mining

and Refining Company at De Beque, Colo., gave the following results:<sup>2</sup>

	Per cent	Per cent	
Total sulfur	1.373	Organic sulfur	0.649
Sulfide and sulfate sulfur	0.724	Humus sulfur	0.644
Sulfide sulfur	0.6375	Resinic sulfur	0.005
Sulfate sulfur	0.0865		

No resinic sulfur was found in the Elko Nevada shale. Resinic sulfur was found in the Green River shale in an amount so small as to be within the limits of experimental error and may be considered as absent in this shale. The organic sulfur varied from 19.2 per cent in the Elko Nevada shale to 49.5 per cent in the Green River formation. The sulfide sulfur varied from 72.6 per cent in the Elko Nevada shale to 37.2 per cent in the Green River formation. In the Mount Logan shale, which contained no resinic sulfur, there was found 47.3 per cent of organic sulfur and 46.4 per cent of sulfide sulfur. The two shales from different parts of the Green River formation are somewhat similar in their sulfur distribution.

<sup>1</sup> Received December 31, 1927.

<sup>2</sup> Harding and Thordarson, *Ind. Eng. Chem.*, 18, 731 (1926).

# A Differential Index of the Coking Power of Coal<sup>1</sup>

## With Reference to Energy Distribution, Agglutination, and Classification

A. W. Coffman<sup>2</sup> and T. E. Layng

UNIVERSITY OF ILLINOIS, URBANA, ILL.

FOR some time the softening and solidifying point of coal has afforded a basis for considerable speculation as to classification and the mechanism of the coking process. Layng and Hathorne<sup>3</sup> listed a large number of coals whose softening and solidification points had been determined, and the authors<sup>4</sup> have also published a paper on the effect of weathering on these critical temperatures. The very nature of the softening and solidification test seems to point towards its possible use in determining the mechanism of the coking process.

By the use of the softening and solidification point determination test previously described by Layng and Hathorne, the authors have arrived at a graphical means of determining an index number called the agglutinating index for any coal. The relative magnitude of this agglutinating index and the distribution of the area beneath the time- $dp/dt$  curve indicates the manner in which coking energy and agglutinating power is distributed in coal. The state of weathering through which coal has passed may be determined by the value of the agglutinating index.

It has also been shown that the agglutinating power of a coal is a function of (1) the rate of heating to which it has been subjected, (2) the conditioning to which it has been subjected, (3) the weathering through which it has passed, and (4) the chemical interactions taking place during plasticity. Under the test conditions stated to produce coke coals must have an agglutinating index of 20 or more.

glass tube set vertically through the furnace. Between the nitrogen bottles and the Pyrex tube an ordinary U-type manometer with a capacity of 2600 mm. of water was inserted in the line. The glass tube was a Pyrex combustion tube 14 mm. in diameter. In this tube a copper spiral 10 cm. long was used to support the coal and the coal column extended for 10 cm. above it.

A standard base-metal Hoskins indicator was used in conjunction with a base-metal thermocouple for indicating the temperature of the coal mass.

### Nature of the Test

**APPARATUS**—The apparatus used for the measurement of the temperature range of plasticity during the carbonization of coal is simple both in form and operation. This apparatus has previously been described by Layng and Hathorne, and the diagram of such an assembly is shown in Plate 1. It consists of a furnace for heating the coal, a constant-head device for supplying a constant flow of nitrogen through the coal mass, a manometer, and a pyrometer for measuring the temperature developed in the furnace.

The original furnaces were merely wire-wound tube furnaces capable of taking a tube with a diameter of about 2.86 cm. The heating unit was about 30.5 cm. in length. This type of furnace was discarded, however, in favor of a vertically mounted wire wound furnace 50.8 cm. long and with an opening of 10.16 cm. diameter. A fan mounted on the furnace extended downward into a copper tube which was open at the top and bottom. Upon being revolved by a small 110-volt motor this fan circulated the air in the furnace to such an extent that it was possible to keep a temperature which was uniform throughout the furnace to  $\pm 4^\circ$  C. The heating of this furnace was controlled by an external variable resistance of nichrome wire.

The constant supply of nitrogen was obtained with a constant head apparatus and a 12-liter bottle. This head was similar to the one used on a Junker gas calorimeter having a head of 1500 mm. of water. At the start the volume of water delivered to the nitrogen bottle was regulated to 40 cc. per minute by a stopcock and not changed thereafter. The gas was taken off the top of the bottle as it was displaced by the incoming water and passed into the bottom of a Pyrex

**MANIPULATION**—After reduction with methanol, the copper gauze spiral was placed in the combustion tube so as to cause the bottom of the coal column to fall about 5 cm. above the center of the furnace. The 20- to 60-mesh coal sample was then poured into the top of the tube and the tube tapped with a wooden stick to pack the coal sample. In this manner a column of coal 10 cm. in length was obtained, a thermocouple being attached to the glass tube, just at the center of the coal mass on the outside of the tube.

The tube was then adjusted in the furnace as shown in the diagram and the gas flow started along with the turning on of the fan and furnace. The temperature in the

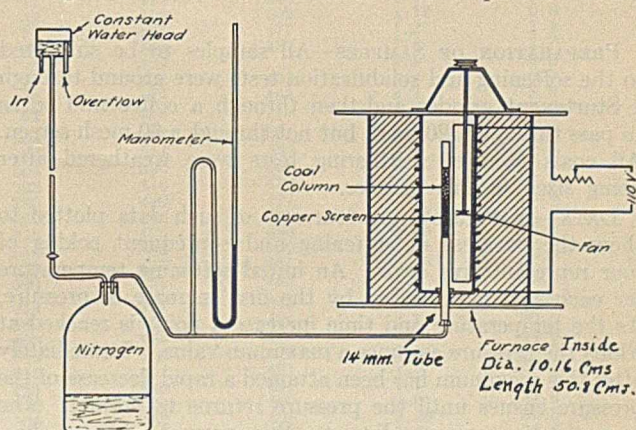


Plate 1—Apparatus

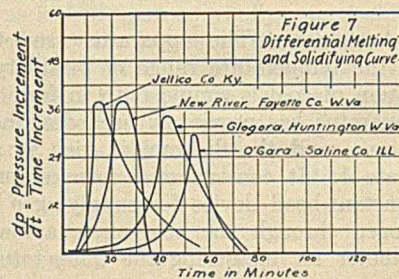
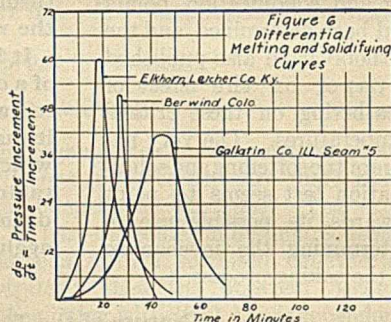
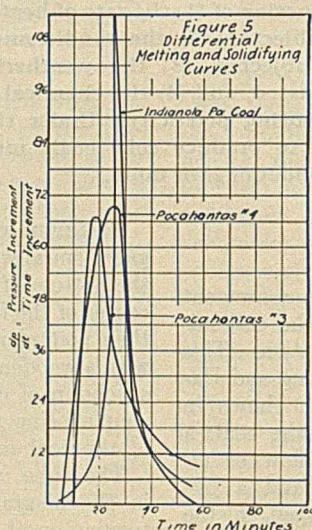
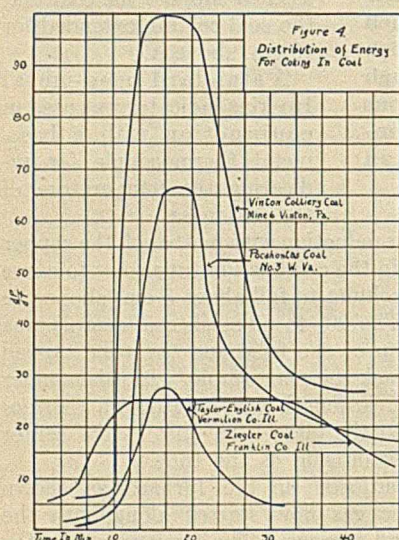
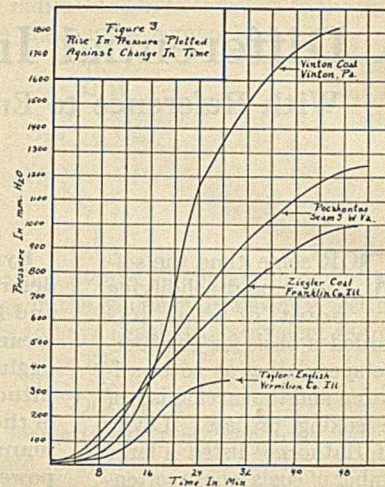
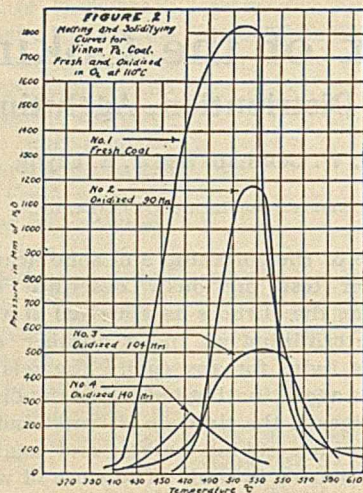
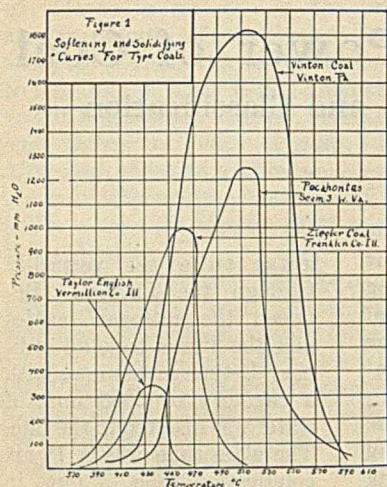
furnace was raised at the rate of  $8^\circ$  to  $10^\circ$  C. per minute till about  $300^\circ$  C. was reached. At this point the resistance was increased so that by the time  $330^\circ$  C. was reached the rate of rise became approximately  $2^\circ$  C. per minute. It is extremely important to maintain the same rate of temperature rise throughout all tests which are to be compared, since variation in rate means considerable variation in initial plasticity and consequent solidification. Time, temperature, and pressure readings were made and recorded at 2-minute intervals.

<sup>1</sup> Presented before the Division of Gas and Fuel Chemistry at the 74th Meeting of the American Chemical Society, Detroit, Mich., September 5 to 10, 1927.

<sup>2</sup> Present address Mellon Institute of Industrial Research, University of Pittsburgh, Pittsburgh, Pa.

<sup>3</sup> *Ind. Eng. Chem.*, **17**, 165 (1925).

<sup>4</sup> *Ibid.*, **19**, 924 (1927).



PREPARATION OF SAMPLES—All samples to be subjected to the softening and solidification tests were ground through a Sturtevant grinder and then through a coffee mill so as to pass through a 20-mesh but not through a 60-mesh screen. All coals used in weathering tests were weathered after being sized in this manner.

DATA—In Figure 1 are four sets of such data plotted to show the progress of softening and consequent coking of four representative coals. An initial softening temperature for each coal is indicated by the first increase in pressure. As the temperature and time increase a point is reached at which the pressure assumes a maximum value. Immediately after this maximum has been attained a rapid decrease of the pressure ensues until the pressure returns to normal. The temperature corresponding to this normal pressure has, in previous publications, been called the "temperature of coke formation."

The effect of weathering on these points has been shown by Layng and Coffman.<sup>4</sup> Figure 2 shows such a set of curves on variously weathered samples of Vinton, Pa., coal. Similar curves have been obtained by the authors on preheating in various atmospheres followed by cooling before carrying out the softening test. The results of these tests are possible of verification and have shown promise of being valuable (1) in aiding in the classification of those coals which soften on heating, (2) in tracing any particular seam

of coal, (3) in determining the particular state of a coal which has been weathered, (4) in determining the effect of conditioning upon a coal.

It is the purpose of this paper to show the application of this test in evaluating the so-called agglutinating power for any coal, and also to establish the idea that the agglutinating value of a coal is not merely the power of a coal to bind a large number of particles together but is the resultant of a large number of governing factors. Chief among these factors which control the agglutinating power of a coal are (1) the rate of heating at which the coal is carbonized, (2) the previous conditioning of the coal, (3) the amount of weathering to which the coal has been subjected, and (4) the chemical interaction taking place between the coal constituents.

#### Value of Temperature-Pressure Curves

A consideration of the original temperature-pressure curves as shown in Figure 1 leads to the conclusion that the point defined as the coke-formation point is relatively unimportant, since it merely marks the end of a very rapid dropping off in pressure. The point of maximum pressure really marks the completion of complex processes chiefly indicated by softening and cell formation, and this cell formation, which is the end or resultant of all the reactions, ending



in the fixation of the mass, accounts for the rapid diminution in pressure which follows.

It therefore seems that the important portion of the temperature-pressure curve falls between the initial softening temperature and the point of maximum pressure, since this is the true range of plasticity. Considering only this portion of the curve, therefore, a graphical study has been carried out which has led to the development of an expression involving these various factors and which we call the "differential" or "agglutinating index."

### Differential Index

The differential index has been derived solely from time-pressure relations between the initial softening point and point of maximum pressure. Taking the same coals shown in Figure 1, the curves of Figure 3 have been plotted using pressure and time as the coordinates. In Figure 4 the data plotted in Figure 3 have been recalculated and replotted. Here the value of  $dp/dt$ , or the ratio of the increment of pressure in millimeters to the increment of time in minutes, has been calculated at regular intervals and this series of values plotted against the time in minutes. In these curves the value of  $dp/dt$  increases with the time until a maximum is reached and then decreases. As a matter of definition for purposes of discussion, this maximum value of  $dp/dt$  for any differential softening curve will be called the "differential index" or "agglutinating index" of the coal.

It is readily seen from such a consideration that any changes in the rate of heating of a coal would greatly affect the value of  $dp/dt$ . Consequently for results of this test to be comparable all data must be obtained using the same rate of heating. As an illustration of the importance of this statement the differential indexes for all coals which have

been run in this laboratory have been calculated. These values, along with the other data and calculated rates of heating, are tabulated in Table I arranged according to increasing index value.

Sangamon County, Ill., coals, Nos. 8 and 55 are out of order according to their known properties. This may be explained by the increased rate of heating which was used—namely, 2.7° and 3.0° C. per minute. Other exceptions in the order of the coals are directly due to the variations in the rate of heating.

Table II—Coals on Which the Rate of Heating Is between 1.0° and 2.0° C. per Minute

DESCRIPTION OF COAL	RATE OF HEATING	
	° C. per min.	$dp/dt$
Castle Gate, Utah, Mine No. 2	1.1	0.3
Franklin Co., Ill., Ziegler No. 1 Mine	1.17	0.8
Williamson Co., Ill., Glen Carbon Hill Mine	1.2	1.1
Franklin Co., Ill., Makitan Mine	1.5	1.7
Saline Co., Ill.	1.9	5.9
Hickory Hill, Gallatin Co., Ill.	1.5	19.3
Pocahontas No. 3, W. Va.	2.0	20.0
Electric Coal Co., Vermilion Co., Ill.	1.15	20.4
O'Gara Coal, Saline Co., Ill.	1.6	22.8
Ziegler, Franklin Co., Ill.	1.88	25.0
Hickory Hill, Gallatin Co., Ill.	1.15	25.0
Moultrie Co., Ill., Lovington Mine	1.15	25.9
Taylor English, Vermilion Co., Ill.	1.95	27.7
Saline Co., Ill., O'Gara Coal	1.2	29.0
Jellico Coal, Ky.	1.4	29.0
Glogora, Huntington, W. Va.	1.4	32.0
Electric Coal, Vermilion Co., Ill.	1.6	34.3
Jellico Coal, Ky.	1.7	36.7
New River, Fayette Co., W. Va.	2.0	37.0
Gallatin Co., Ill., Seam No. 5	1.4	40.2
Berwind, Colo.	1.5	50.7
Elkhorn, Letcher Co., Ky.	1.9	60.8
Elkhorn, Letcher Co., Ky.	1.95	60.8
Pocahontas, W. Va.	1.8	66.6
Pocahontas, W. Va.	1.8	69.3
Indianola, Pa.	1.95	115.0

In Table II are given those coals whose rate of heating was between 1.0° and 2.0° C. per minute with their values of  $dp/dt$ . Here the coals arrange themselves in a natural

Table I—Tabulation of  $dp/dt$  with Rate of Heating and Critical Temperatures of Plasticity

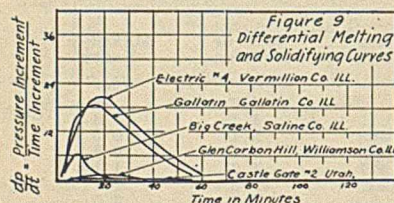
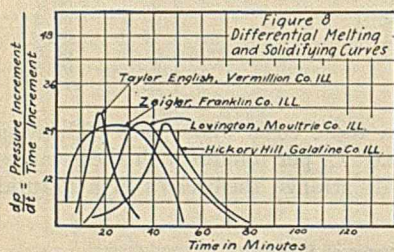
DESCRIPTION OF COAL	TEMPERATURE OF					
	SOFTENING TEMPERATURE ° C.	MAXIMUM PRESSURE Mm.	MAXIMUM PRESSURE ° C.	COKE FORMATION ° C.	RATE OF HEATING ° C. per min.	MAXIMUM VALUE $dp/dt$
Tioga, Colo., Kebler No. 2	...	...	...	...	3.2	0
Castle Gate, Utah, No. 2	...	...	...	...	1.1	0.3
Knox Co., Ill., Peterson Co.	404	11	425	463	3.1	0.5
Franklin Co., Ill., Ziegler 1	372	32	412	539	1.17	0.8
Williamson Co., Ill., Glen Carbon Hill	409	71	445	477	1.2	1.1
Franklin Co., Ill., Makitan	374	60	406	437	1.5	1.7
Peoria Co., Ill., Edwards Silver Creek	405	5	429	...	2.5	3.5
Saline Co., Ill., Big Creek	397	60	435	465	1.9	5.9
Warren Co., Ill., Mine No. 4	395	90	433	463	3.2	8.8
Macon Co., Ill., Macon Mine	412	64	438	...	3.8	10.0
Hickory Hill, Gallatin Co., Ill.	356	504	404	491	1.5	19.3
Pocahontas Seam No. 3, W. Va.	430	370	514	540	2.0	20.0
Electric Coal, Vermilion Co., Ill.	361	504	390	450	1.15	20.4
Fulton Co., Ill., Mine No. 5	405	228	446	472	4.2	22.5
O'Gara Coal, Saline Co., Ill.	350	780	480	497	1.6	22.8
Ziegler, Franklin Co., Ill.	378	998	465	512	1.98	25.0
Hickory Hill, Gallatin Co., Ill., Seam 5	357	735	425	480	1.15	25.0
Moultrie Co., Ill., Lovington	343	812	395	430	1.15	25.9
Taylor English, Vermilion Co., Ill.	378	350	436	465	1.95	27.7
Saline Co., Ill., O'Gara Coal Co.	377	660	451	463	1.2	29.0
Jellico Coal, Ky.	375	944	477	517	1.4	29.0
Sangamon Co., Ill., Mine No. 55	392	580	455	475	2.7	30.0
Sangamon Co., Ill., Mine No. 8	398	400	455	470	3.0	32.0
Glogora, Huntington, W. Va.	366	842	460	495	1.4	32.0
Electric Coal, Vermilion Co., Ill.	349	911	442	491	1.6	34.3
Jellico Coal, Ky.	372	754	420	491	1.7	36.7
New River, Fayette Co., W. Va.	385	1370	520	569	2.0	37.0
Elkhorn Coal, Letcher Co., Ky.	400	300	457	505	2.59	37.5
McLean Co., Ill.	402	555	461	485	3.4	38.3
Fulton Co., Ill., Silver Creek	370	280	425	452	2.4	40.0
Gallatin Co., Ill., Seam No. 5	354	833	425	475	1.4	40.2
Franklin Co., Ill., West Frankfort Mine	387	915	467	481	2.4	40.5
Knox Co., Ill., Milan Mine	408	333	446	470	4.2	41.0
Montgomery Co., Ill., Mine No. 8	425	1178	545	583	2.3	45.0
Knox Co., Ill., Adcock Mine	402	475	438	475	4.3	48.5
Berwind, Colo.	400	662	442	478	1.5	50.7
Sangamon Co., Ill., Peerless Mine	381	618	414	455	2.8	58.5
Henry Co., Ill., Rex Mine	404	455	436	462	3.0	60.0
Elkhorn, Letcher Co., Ky.	385	755	431	480	1.9	60.8
Elkhorn, Letcher Co., Ky.	400	378	427	555	1.95	60.8
Tazewell Co., Ill., Groveland No. 2 Mine	390	505	412	445	2.9	66.5
Pocahontas, W. Va.	418	1244	518	600	1.8	66.6
Pocahontas, W. Va.	428	1300	505	597	1.8	69.3
Sangamon Co., Ill., Mine No. 54	395	810	431	483	2.2	77.0
Vinton, Mine 6, Cambria Co., Pa.	403	1800	513	595	2.7	100.0
Indianola, Pa.	373	931	418	532	1.95	115.0

order according to properties with only one or two exceptions. One sample of Pocahontas No. 3 coal shows a low value of  $dp/dt$  because this coal was in a different state of weathering than the other sample of Pocahontas No. 3 coal. Figures 5 to 9 show the differential curves for these coals. This affords, perhaps, a better means of classification than the use of the initial softening temperature. The initial softening temperature is not affected by the rate of heating to which a coal is subjected, whereas the agglutinating power and agglutinating index are affected to a large degree by changes in the rate of heating. By way of illustration, in a classification according to the differential index determined with the indicated rate of heating on coal samples of varying degrees of freshness, softening coals would be divided into:

COAL	INDEX
(1) Illinois bituminous	20 to 40
(2) Semibituminous	30 to 50
(3) Eastern bituminous	50 to 125

### Energy Distribution

A consideration of the manner of derivation of these curves leads to the idea that they picture the distribution of energy in the coal. It is a recognized fact that during the process of carbonization chemical reactions occur at the same time that softening occurs. If these reactions produce fixed gases,



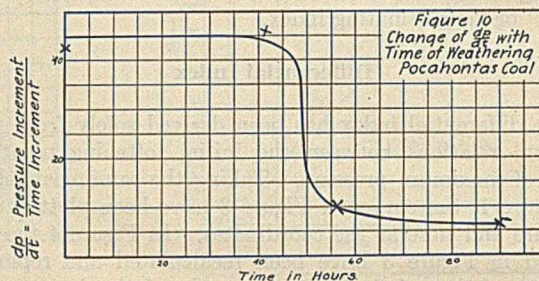
as they do, and the back pressure of these gases enters into the pressure measurements as well as the resistance to flow which the plastic mass offers to an inert gas with constant head, then an indication of the distribution of the chemical energy of the coal may be obtained from either type of experiment. It now becomes apparent that the differential index indicates the manner in which the energy in a coal is proportioned over the plastic range. When the differential is plotted in this manner, giving symmetrical curves, it is apparent that they assume the form of Maxwellian energy-distribution curves.

Figures 5 to 9 show that the coking energy is distributed over a temperature and time range for this particular rate of heating used. However, in each coal the energy is distributed in a different manner, but coals of the same type have approximately equal total quantities of energy represented by the areas beneath the curves.

Furthermore, from the appearance of these curves it seems that for a coal to coke two conditions must be fulfilled: (1) The differential index must be above a value of 20; (2) the total energy must be used in a comparatively short time giving rise to a peak in the curve. It appears that these two conditions may be fulfilled in the case of the more poorly coking coals by varying the four factors which have been named as governing the agglutinating value. Thus, by a variance in one or more of these factors it should be possible to increase the maximum value of  $dp/dt$  so as to cause a different distribution of energy followed by the formation of an energy peak. The following paragraphs illustrate the manner in which these factors influence the agglutinating index of a coal.

### Effect of Rates of Heating

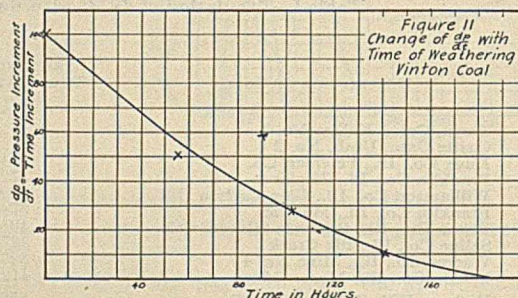
As an example of the first method of increasing the value of the differential index, data given by Layng and Hathorne<sup>5</sup> have been calculated to the above basis (Table III). The method of obtaining the original data was slightly different from the standard in that no nitrogen was passed through the coal mass. This method of determining  $dp/dt$  is really of greater value, since it considers only the pressures of the gas



liberated and thus comes more nearly to measuring the true energy index of the coal. However, these data are comparable one with another and check the old method as to the softening and solidifying temperatures, differing only in the magnitude of  $dp/dt$  which is somewhat higher by this method than by the original. These data indicate very clearly that increasing the rate of heating increases the value of  $dp/dt$  to an appreciable degree.

### Conditioning Treatments

Layng and Coffman<sup>4</sup> tabulated the effects of preheating several coals in various atmospheres. These results have been retabulated and  $dp/dt$  calculated as shown in Table IV showing a distinct change in the differential index upon a change in the nature of the coal by treatment. In some cases,



for example, Gallatin County, Ill., coal and O'Gara, Saline County, Ill., coal, the nature of the coal has been changed to such an extent that the value of  $dp/dt$  is appreciably increased over the value for the fresh coal.

Table III—Data on Coals Showing Effects of Various Rates of Heating

SOFTENING TEMPERATURE ° C.	MAXIMUM PRES-SURE Mm.	TEMPERATURE OF		COKE FORMATION ° C.	RATE OF HEAT-ING ° C. per min.	MAXIMUM VALUE $dp/dt$
		MAXIMUM PRESSURE ° C.	FORMATION ° C.			
SALINE CO., ILL., COAL						
390	25	513	..	1.5	1.0	
395	60	435	465	1.9	5.9	
395	900	468	520	2.4	46.0	
395	475	450	480	4.3	125.0	
395	220	505	528	9.0	50.0	
POCAHONTAS NO. 3, W. VA., COAL						
425	1500	485	510	0.73	24.1	
430	370	515	535	2.0	20.0	
430	950	510	548	2.8	139.0	
430	1250	510	548	4.8	167.0	
425	1250	508	550	5.0	228.0	
ELKHORN, LETCHER CO., KY., COAL						
404	120	428	458	1.33	8.9	
402	297	458	505	2.59	37.5	
402	466	473	500	3.00	38.9	
402	446	446	490	3.06	133.3	
417	560	470	517	7.14	250.0	

<sup>5</sup> Unpublished thesis, University of Illinois, Urbana, Ill.

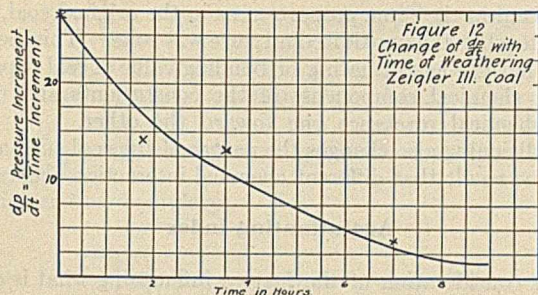


Figure 12  
Change of  $\frac{dp}{dt}$  with  
Time of Weathering  
Zeigler Ill. Coal

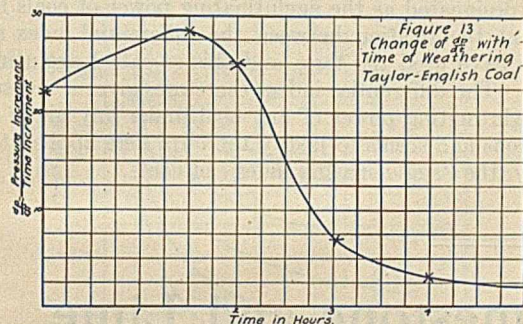


Figure 13  
Change of  $\frac{dp}{dt}$  with  
Time of Weathering  
Taylor-English Coal

## Weathering

Weathering is one of the commonest means of changing the chemical nature of coal, and it is a well-established fact that such a change is detrimental to the coking power of coals. The authors<sup>4</sup> have listed the effects of accelerated weathering on the softening and solidification points of coal. Table V lists these values with the rates of heating and the differential index. It is seen that for each coal the value of the differential index decreases with increase in amount of weathering, showing that the coking energy and agglutinating value of coals are decreased in weathering.

Figures 10 to 14 indicate the change in the index with the length of weathering for the five coals for which data have been obtained.

## Chemical Interactions

This fourth factor governing the agglutinating power of a coal is so closely allied with the other three that it is almost a part of each. Weathering, conditioning, and rates of heating of coal all play an important part in determining just what reactions shall occur during the period of plasticity.

The bituminic material in coal forms the bonding or agglu-

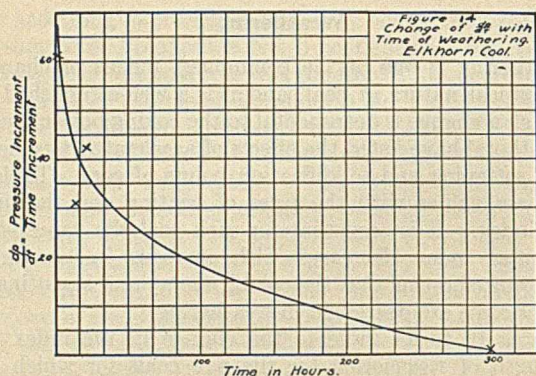
Table IV—Effect of Preheating on Softening of Coals

SOFTENING TEMPERATURE ° C.	MAXIMUM PRESSURE Mm.	TEMPERATURE OF MAXIMUM PRESSURE ° C.	COKE FORMATION ° C.	RATE OF HEATING ° C. per min.	TREATMENT OF SAMPLE	MAXIMUM VALUE $\frac{dp}{dt}$
JELICO, KY., COAL						
372	754	420	491	1.7	Fresh coal	36.7
375	480	452	490	1.6	Preheated and cooled in N <sub>2</sub> (350° C.)	15.0
377	780	439	473	1.5	Preheated and cooled in N <sub>2</sub> (300° C.)	37.5
386	94	390	420	2.1	Preheated and cooled in air (250° C.)	7.5
361	104	410	444	1.8	Preheated and cooled in air (200° C.)	15.5
374	550	424	474	1.6	Preheated and cooled in air (150° C.)	17.0
O'GARA, SALINE CO., ILL., COAL						
350	780	480	497	1.6	Fresh coal	22.8
396	40	415	458	1.5	Preheated and cooled in N <sub>2</sub> (350° C.)	2.2
383	40	400	445	1.6	Preheated and cooled in N <sub>2</sub> (250° C.)	1.9
367	12	394	510	1.5	Preheated and cooled in air (350° C.)	0.3
350	206	402	488	2.1	Preheated and cooled in air (250° C.)	14.6
380	386	407	470	2.2	Preheated and cooled in air (200° C.)	36.0
380	560	420	466	1.9	Preheated and cooled in air (150° C.)	25.2
ELECTRIC COAL, VERMILION CO., ILL.						
349	911	442	491	1.6	Fresh coal	34.3
390	17	413	434	1.0	Preheated and cooled in N <sub>2</sub> (350° C.)	1.0
349	530	404	451	1.4	Preheated and cooled in N <sub>2</sub> (250° C.)	25.0
HICKORY HILL, GALLATIN CO., ILL.						
356	504	404	491	1.5	Fresh coal	19.3
350	454	410	434	1.8	Preheated and cooled in N <sub>2</sub> (300° C.)	24.0
345	314	396	435	1.4	Preheated and cooled in N <sub>2</sub> (350° C.)	16.6

Table V—Effect of Accelerated Weathering on Softening of Coal

SOFTENING TEMPERATURE ° C.	MAXIMUM PRESSURE Mm.	TEMPERATURE OF MAXIMUM PRESSURE ° C.	COKE FORMATION ° C.	RATE OF HEATING ° C. per min.	MAXIMUM VALUE $\frac{dp}{dt}$	TREATMENT OF SAMPLE <sup>a</sup>
TAYLOR ENGLISH, VERMILION CO., ILL.						
378	350	436	455	1.9	22.2	Original
382	430	432	485	1.85	28.0	Oxidized 1.5 hours
383	324	418	450	1.9	25.0	Oxidized 2 hours
388	93	409	470	1.93	6.8	Oxidized 3 hours
394	13	414	445	1.9	3.0	Oxidized 4 hours
ZIEGLER, FRANKLIN CO., ILL.						
378	998	465	508	1.88	27.2	Original
399	350	467	507	1.4	14.2	Oxidized 1.75 hours
396	230	438	470	1.86	12.7	Oxidized 3.5 hrs.
376	74	426	477	2.2	3.6	Oxidized 7 hours
ELKHORN COAL, LETCHER CO., KY.						
385	755	431	480	1.9	60.8	Original
388	510	434	490	2.1	33.0	Oxidized 15 hours
395	324	438	483	2.4	43.0	Oxidized 20 hours
398	23	430	453	1.9	0.3	Oxidized 300 hours
POCAHONTAS COAL NO. 3, W. VA.						
418	1244	518	600	1.85	42.0	Original
429	1385	545	495	2.1	46.0	Oxidized 42 hours
438	240	431	570	2.3	10.0	Oxidized 56 hours
434	174	495	535	1.65	6.5	Oxidized 90 hours
VINTON, MINE 6, CAMBRIA CO., PA.						
403	1800	513	595	2.7	100.0	Original
418	1289	535	590	2.2	45.0	Oxidized 56 hours
405	1172	530	584	2.2	59.4	Oxidized 90 hours
453	473	556	600	2.3	27.1	Oxidized 104 hours
417	246	478	540	2.5	10.4	Oxidized 140 hours

<sup>a</sup> Temperature of oxidation 110° C. in all cases.



tinating substance. Parr<sup>6</sup> has shown that oxidation destroys the coking power of a coal; likewise that oxidized bituminic and cellulosic materials or cellulosic material alone, oxidized

<sup>6</sup> *Ind. Eng. Chem.*, **18**, 640 (1926).

and mixed in the same proportion as in the original coal, will not coke while the unoxidized mixture will coke. This means, then, that the agglutinating or bonding value of coal depends on the chemical components of the constituents and upon their chemical reactivity one toward the other.

Conditioning also changes the nature of the coal substance, with the result that different chemical interaction occurs.

### Agglutinating Index

This consideration of the factors influencing what is commonly designated as the agglutinating power of coals makes apparent the relation between the differential index as the writers have used the term and this so-called agglutinating power. The differential index, therefore, gives a measure of the agglutinating power of any coal under any given set of conditions and seems to justify the term here applied to it—namely, the "agglutinating index" of coal.

## Flow of Heat through Limestone and Lime<sup>1</sup>

R. T. Haslam<sup>2</sup> and V. C. Smith

DEPARTMENT OF CHEMICAL ENGINEERING, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASS.

THE work of Gurney and Lurie<sup>3</sup> on the rate of heating of solids made simple the complicated mathematics of this aspect of heating, but it was limited to cases of simple heating. No attempt was made to find a method applicable to those cases in which heat is utilized or liberated in effecting some chemical or physical reaction. The calcination of limestone is an example of such a process. It was felt, however, that their method was capable of extension to this type if certain constants were determined empirically.

This paper represents the application of their method to the rate of heating as well as to the rate of dissociation of

nature of the equations has thus far limited a rigorous solution to but one case—that of the semi-infinite solid—and this, unfortunately, the least attainable in practice.

### Heating of Semi-infinite Blocks

If a semi-infinite block of limestone is being heated to a temperature above that at which it dissociates into lime, we may, as in Figure 1, designate the distance below the surface by the  $x$  coordinate axis, and the temperature by the  $y$  axis. The extent of dissociation is denoted by  $E$  and the subscripts 1 and 2 refer to lime and limestone, respectively.

The equations of linear heat conduction are

$$\frac{\delta t}{\delta \theta} = \alpha_1^2 \frac{\delta^2 t}{\delta x^2} \quad (\text{for } x < E) \quad (1)$$

$$\frac{\delta t}{\delta \theta} = \alpha_2^2 \frac{\delta^2 t}{\delta x^2} \quad (\text{for } x > E) \quad (2)$$

where  $\alpha^2 = \frac{K}{SC}$  = diffusivity  
 $t$  = temperature  
 $\theta$  = time  
 $K$  = thermal conductivity  
 $S$  = density  
 $C$  = specific heat

Initial conditions:

$$\text{For } \theta = 0, t = t_0 \quad (3)$$

Boundary conditions

$$(a) \text{ At the exposed surface—} \\ \text{For } x = 0 \text{ and } \theta \geq 0, t = t_s \quad (4)$$

$$(b) \text{ At very great depths—} \\ \text{For } x = \infty \text{ and } \theta \geq 0, t = t_0 \quad (5)$$

$$(c) \text{ At the dissociation boundary—} \\ \text{For } x = E \text{ and } \theta > 0, t_1 = t_D = t_2 = \text{constant} \quad (6)$$

limestone. More particularly, slabs of limestone have been heated under conditions in which there was no dissociation and again where dissociation did occur. The temperature-time effect was determined by thermocouples embedded at known distances from the exposed faces. These data have not only furnished the surface coefficient of heat transfer for limestone, but along with the Gurney-Lurie plots afford direct application of the plots to the more complicated process mentioned above.

It appeared desirable to derive a rigorous solution for the rate of dissociation which would apply to different shapes as well as to different surface conditions. The complicated

<sup>1</sup> Received June 21, 1927.

<sup>2</sup> Present address: Standard Development Co., 26 Broadway, New York, N. Y.

<sup>3</sup> *Ind. Eng. Chem.*, **15**, 1170 (1923).

If the dissociation boundary of unit area moves the distance  $dE$  in the time  $d\theta$ , limestone of volume  $dE$  is dissociated, and a quantity of heat  $Q_D S_2 dE$  is absorbed ( $Q_D$  denotes the heat of dissociation into lime of unit mass of limestone).

From Newton's law of heat flow the equation of continuity becomes

$$-K_1 \left( \frac{\delta t}{\delta x} \right)_{E-D} d\theta = Q_D S_2 dE - K_2 \left( \frac{\delta t}{\delta x} \right)_{E+D} d\theta$$

or,

$$\frac{dE}{d\theta} = \frac{1}{Q_D S_2} \left[ K_2 \left( \frac{\delta t}{\delta x} \right)_{E+D} - K_1 \left( \frac{\delta t}{\delta x} \right)_{E-D} \right] \quad (7)$$

where  $\left( \frac{\delta t}{\delta x} \right)$  is the temperature gradient on either side of the dissociation boundary.

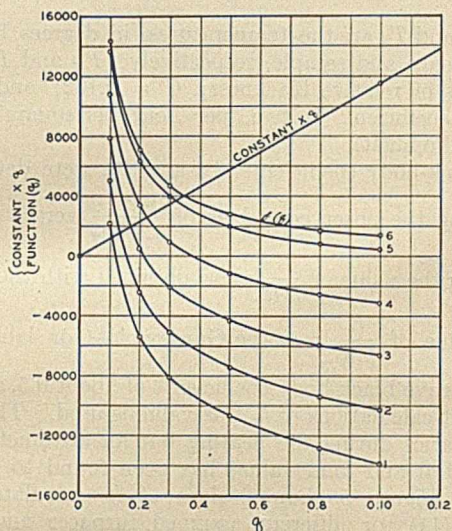


Figure 2—Graphical Solution of Equation—Constant  $\times q = f(q)$   
 $t_s = 1900^\circ \text{F.}$   
 Curve 1:  $t_0 = 0^\circ \text{F.}$ ; Curve 2:  $t_0 = 400^\circ \text{F.}$ ; Curve 3:  $t_0 = 800^\circ \text{F.}$ ; Curve 4:  $t_0 = 1200^\circ \text{F.}$ ; Curve 5:  $t_0 = 1600^\circ \text{F.}$ ; Curve 6:  $t_0 = 1700^\circ \text{F.}$

The particular solutions of equations (1) and (2), together with the initial and boundary conditions, lead to the relationship

$$E = q\sqrt{\theta}$$

and

$$\frac{dE}{d\theta} = q/2\sqrt{\theta} \quad (8)$$

where  $q$  is a proportionality constant.

Equation (7) is used to determine the value of  $q$ , for it may be expressed in the following form:

$$\frac{\sqrt{\pi}}{2} Q_D S_2 q = b_1(t_s - t_D) \frac{e^{-q^2/4\alpha_1^2}}{\sqrt{\pi} \int_0^{\beta_1} e^{-\beta_1^2} d\beta} - b_2(t_D - t_0) \frac{e^{-q^2/4\alpha_2^2}}{1 - \frac{2}{\sqrt{\pi}} \int_0^{\beta_2} e^{-\beta_2^2} d\beta} \quad (9)$$

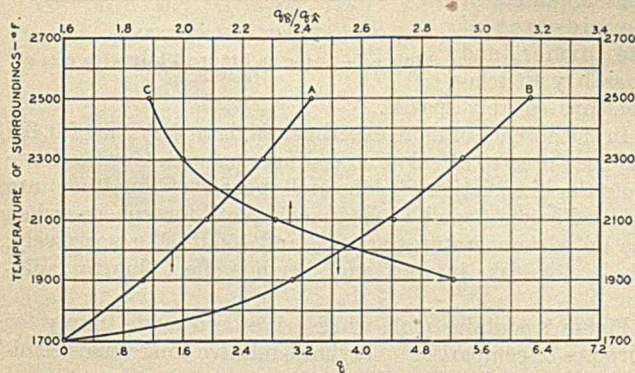


Figure 3—Plot of Surface Temperature vs.  $q$  for Equation— $E = q\sqrt{\theta}$  Inches—with Dissociation  
 Curve A:  $t_0 = 80^\circ \text{F.}$ ; Curve B:  $t_0 = 1600^\circ \text{F.}$ ; Curve C: ratio  $q_B/q_A$

where  $b = \sqrt{KSC}$  and  $\beta = q/2\sqrt{\alpha^2}$

A graphical method is probably best in the solution of equation (9), for we may express it as

$$\text{Constant} \times q = f(q)$$

Plots of (constant  $\times q$ ) versus  $q$ , and  $f(q)$  versus  $q$  intersect at one point for each assumed case and each intersection furnishes the value of  $q$  to be used in equation (8).

Figure 2 shows a set of curves for a surface temperature of  $1900^\circ \text{F.}$  and six different initial temperatures. Figure 3 shows how the constant  $q$  varies when the surface temperature varies from  $1700^\circ \text{F.}$ , the assumed dissociation temperature, to  $2500^\circ \text{F.}$  The effect of preheating is indicated by a plot of the ratio of  $q$  with initial temperatures of  $1600^\circ$  and  $80^\circ \text{F.}$  for different surface temperatures. It is seen that the effect of preheating decreases as the surface temperature increases.

Increasing the initial or surface temperature has been shown to increase the rate of travel of the dissociation isothermal, when dissociation occurs. We should expect the rate of travel of this isothermal to increase also with increased surface or initial temperature. Curves A and B of Figure 4 are plots of surface temperature versus the proportionality constant  $q$  in equation

$$R = q'\sqrt{\theta}$$

where  $R$  is the distance traveled by the dissociation isothermal, assuming no dissociation.

These values were calculated from the equation

$$t_D = t_s + (t_0 - t_s) \frac{2}{\sqrt{\pi}} \int_0^{R/2\sqrt{\alpha^2\theta}} e^{-\beta^2} d\beta \quad (10)$$

where  $t_D$  is the dissociation temperature,  $t_0$  and  $t_s$  the initial and surface temperatures, respectively.

In Figure 4 are plotted also the ratios of the proportionality constants without and with dissociation for the same initial and surface temperatures. It is seen that the ratio is practically constant at low initial temperatures (curve C), while with considerable preheat ( $1600^\circ \text{F.}$ ) the ratio decreases with increasing surface temperatures (curve D).

#### Applications to Limited Shapes

From the standpoint of practical significance the treatment of the semi-infinite solid just completed is of doubtful value. It is well known that, as burned, limestone is in very limited sizes.

The ease with which the calculations for the semi-infinite shape are handled compared with the almost impossible nature of the others is the only justification for this method.

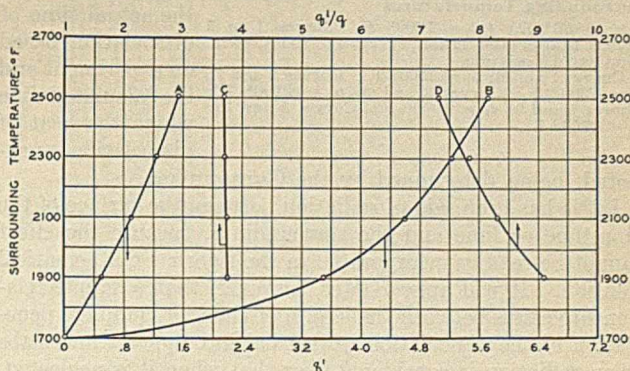


Figure 4—Plot of Surface Temperature vs.  $q'$  for Equation— $R = q'\sqrt{\theta}$  Inches—without Dissociation  
 Curve A:  $t_0 = 80^\circ \text{F.}$ ; Curve B:  $t_0 = 1600^\circ \text{F.}$ ; Curves C and D: Ratio of constants without and with dissociation at  $80^\circ$  and  $1600^\circ \text{F.}$ , respectively

It is hoped that some simple calculations for limited shapes might ultimately be worked out.

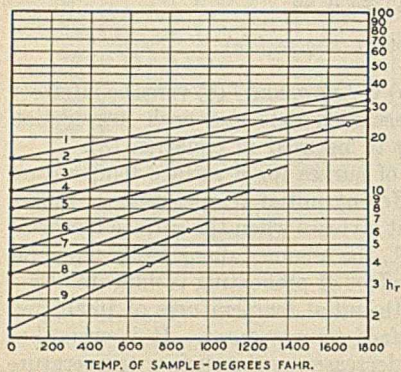


Figure 5—Values of  $h_r$  for Equation— $q/\theta = h_r A (t_w - t_p)$  ( $P_w$  and  $P_p$  assumed 0.5)

Curve 1:  $t_w = 2400^\circ \text{F.}$ ; Curve 2:  $t_w = 2200^\circ \text{F.}$ ; Curve 3:  $t_w = 2000^\circ \text{F.}$ ; Curve 4:  $t_w = 1800^\circ \text{F.}$ ; Curve 5:  $t_w = 1600^\circ \text{F.}$ ; Curve 6:  $t_w = 1400^\circ \text{F.}$ ; Curve 7:  $t_w = 1200^\circ \text{F.}$ ; Curve 8:  $t_w = 1000^\circ \text{F.}$ ; Curve 9:  $t_w = 800^\circ \text{F.}$

at but the two opposite faces. Heat flow was thus for the most part in but one dimension through the specimen. The heat was supplied by an electric carbon resistance furnace which was capable of close regulation.

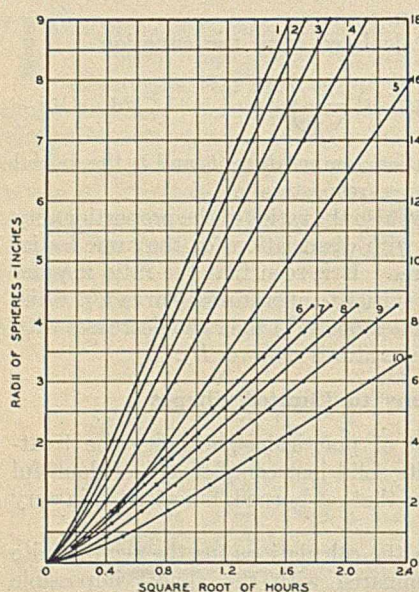


Figure 6—Plot of Complete Penetration vs. Time for Spheres of Limestone with Different Surrounding Temperatures

$t_0 = 80^\circ \text{F.}$ ;  $t_D = 1700^\circ \text{F.}$  Curves 1 to 5 neglect heat of dissociation; curves 6 to 10 represent complete dissociation.

Curves 1 and 6:  $t_s = 2500^\circ \text{F.}$ ; Curves 2 and 7:  $t_s = 2300^\circ \text{F.}$ ; Curves 3 and 8:  $t_s = 2100^\circ \text{F.}$ ; Curves 4 and 9:  $t_s = 1900^\circ \text{F.}$ ; Curves 5 and 10:  $t_s = 1750^\circ \text{F.}$

lected, being determined by the Gurney plots.

Little has been said of radiation between the surface of the limestone or lime and the surroundings, because the effect cannot be readily incorporated in the rigorous mathematical solution. It will appear later, however, that a simple relationship exists between the length of time for complete penetration of the dissociation isothermal into spheres and slabs when radiation is considered over that when it is neglected.

The surface coefficient of heat transfer between the sample and its surroundings,  $h_{c+r}$ , is an important factor in the rate of heating of any solid. Consequently, experiments

### Experimental Part

Slabs of limestone  $1\frac{1}{2}$  by 2 by 4 inches were used. Holes of  $\frac{1}{16}$  inch diameter were drilled parallel to and at different distances from the "exposed faces." Thermocouples were threaded through these holes with the hot junction equidistant from the ends of the specimen. The specimen was then carefully placed in a block of insulating brick so designed as to permit direct heating

of the specimen. The temperature of the furnace was determined optically. At a given time the specimen in its block was placed in the furnace and the temperature-time records were obtained with a potentiometer.

Experiments were made both below and above the dissociation temperature. The former were used to establish the magnitude of the black body coefficient; the latter have been used to establish the relationships between the actual time of dissociation and the calculated time where the heat of dissociation is neglected, being determined by the Gurney plots.

Little has been said of radiation between the surface of the limestone or lime and the surroundings, because the effect cannot be readily incorporated in the rigorous mathematical solution. It will appear later, however, that a simple relationship exists between the length of time for complete penetration of the dissociation isothermal into spheres and slabs when radiation is considered over that when it is neglected.

were made to determine this coefficient. The convection coefficient,  $h_c$ , is negligible, if it has any value at all.

Assuming that, under the conditions of experiment, we had essentially two parallel planes, we may express the value  $h_r$  in the form

$$h_r = \frac{C}{\left(\frac{1}{P_w} - \frac{1}{P_p} - 1\right)(t_w - t_p)} \left[ \left(\frac{T_w}{100}\right)^4 - \left(\frac{T_p}{100}\right)^4 \right] \quad (11)$$

where  $T_w$  and  $T_p$  are the temperatures, in degrees Reaumur of the furnace and sample, respectively;  $P_w$  and  $P_p$ , their coefficients of relative blackness;  $C = 0.162$ ; and  $h_r$ , the radiation coefficient (B. t. u. per hour per square foot per degree Fahrenheit).

The black-body coefficients,  $P_w$  and  $P_p$ , were determined by plotting the observed values of  $\frac{t_s - t}{t_s - t_0}$  versus  $\frac{\alpha^2 \theta}{R^2}$  and comparing the value of  $\frac{K}{h_r R}$  thus obtained with the extrapolated value of  $\frac{K}{h_r R}$  from the Gurney plots for slabs. Such

a method gave black-body coefficients of about 0.5, and in all subsequent calculations of  $h_r$  this value is used. The coefficient  $h_r$  varies during the heating but an arithmetic mean of the initial and final values has been found to be quite accurate. Figure 5 shows values of  $h_r$  calculated from equation (11) for different assumed furnaces and charge temperatures.

Table I contains data for a slab which has been heated from opposite sides at  $1900^\circ \text{F.}$  A ratio of 0.425 is obtained when these

data are compared with the time of penetration of the dissociation boundary to the midplane as calculated from the Gurney-Lurie plots, assuming no dissociation. This ratio is greater than that calculated under similar conditions for the semi-infinite solid, which is 0.267. The difference is attributed to the adiabatic conditions obtaining at the midplane of the former, and possibly to relationships entirely spatial.

In the absence of more experimental data the ratio of 0.425 has been used to calculate in conjunction with Gurney-Lurie plots the dissociation of slabs and spheres of limestone into lime. Figures 6 and 7 show such plots for spheres when the initial temperatures are  $80^\circ$  and  $1600^\circ \text{F.}$ , respectively. These plots take into account the time effect due to radiation.

Figure 8 contains plots which have been made simply for purposes of comparison. It shows relative time versus semi-thickness of slabs, or radii of spheres, for (a) penetration of dissociation isothermal, neglecting and not neglecting radiation; (b) actual penetration of the dissociation isothermal

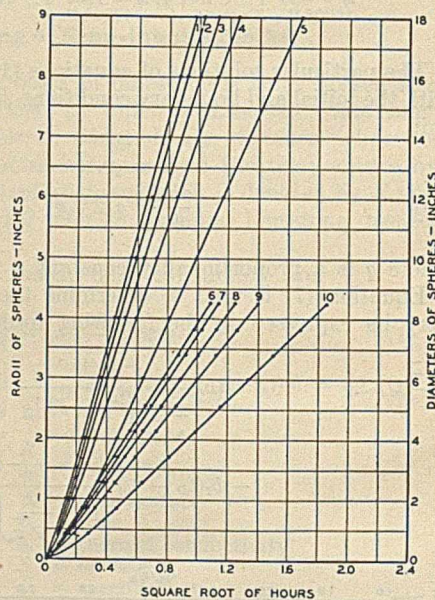


Figure 7—Same as Figure 6 but with a  $t_0$  of  $1600^\circ \text{F.}$

Table I—Heat Flow Data for Slab Heated to 1900° F.

Thickness of sample	1.90 inches		
Initial uniform temperature	77° F.		
Average furnace temperature	1900° F.		
Thermocouple	1	2	3
Distance from hot face, inches	0.205	0.47	0.835
TIME	TEMPERATURE		
Minutes	° F.	° F.	° F.
0	77	77	77
5	602		
6		426	
8			376
9		595	
9.5	912		
11			513
12	1044		
13		795	
15			714
16	1216		
17		986	
19			873
22	1373		
23		1137	
25			1094
26	1449		
27		1287	
29			1222
33	1548		
34		1434	
36			1386
37	1591		
38		1494	
40			1461
41	1627		
42		1548	
44			1521
49	1665		
50		1618	
52			1605
60	1705		
61		1665	
63			1663
70	1722		
71		1679	
73			1674
81	1751		
82		1684	
84			1681
91	1773		
92		1686	
94			1683
102	1792		
103		1692	
105			1686
113	1810		
114		1701	
116			1686
126	1834		
127		1713	
129			1686
136	1834		
137		1722	
139			1686

semi-thickness of slabs or the radius of spheres while *a* and *b* are constants.

Another method of attack, and one which is possibly the most valuable for direct application of the Gurney plots to the determination of relative times of dissociation, is by what may be called a "dissociation diffusivity." Gurney has defined "relative time" by the expression  $\frac{\alpha^2 \theta}{R^2}$ . We may extend this to include dissociation in the following manner:

$$\frac{\alpha_w^2 \theta}{R_w^2} = \frac{\alpha_0^2 \theta}{R_0^2}$$

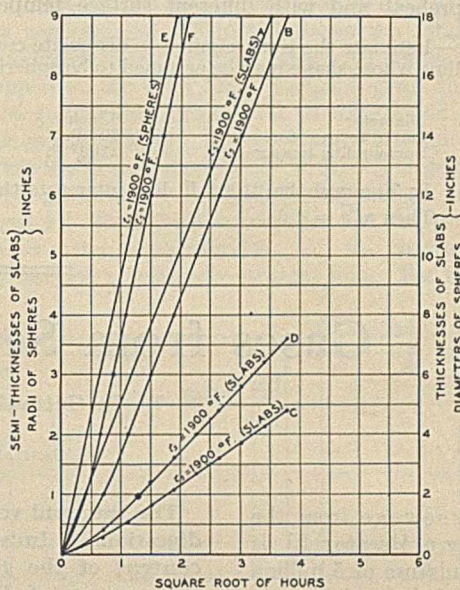


Figure 8—Plot of Complete Penetration vs. Time at  $t_0 = 80^\circ \text{F.}$  for Slabs and Spheres

Curve A: no radiation assumed; Curve B: with radiation; Curve C: based on ratio from semi-infinite shape with radiation; Curve D: based on experimental data; Curve E: no radiation assumed; Curve F: with radiation; Curves A, B, E, and F neglect heat of dissociation

on the ratio basis as found by experiment, as well as the calculated ratio for the semi-infinite block.

It is probably of interest to note that, as plotted, radiation at the surface shifts the curves by an equal amount for all thicknesses except the very small ones, and that a relationship of the form

$$R = a\sqrt{\theta} + b$$

can be assigned to each curve. In this equation *R* is the

where  $\alpha_0^2$  is the diffusivity of limestone,  $R_w$  and  $R_0$  are the semi-thicknesses or radii of slabs or spheres with and without dissociation, and  $\alpha_w^2$  is "dissociation diffusivity."

On the basis of the assumption that there is a definite ratio between the complete penetration in the same time with and without dissociation and that this ratio may be assumed constant over the ranges of preheat or surface temperatures encountered, the "dissociation diffusivity" is calculated from equation (13), and is capable of direct application

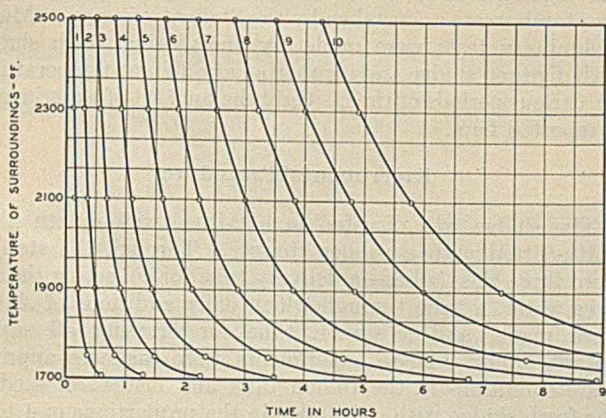


Figure 9—Plot of Time of Dissociation vs. Surrounding Temperatures for Spheres of Limestone  
Initial temperature— $t_0 = 80^\circ \text{F.}$  Curve numbers are diameters in inches

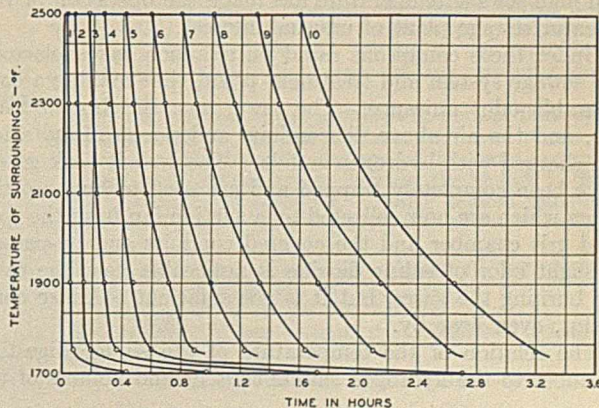


Figure 10—Plot of Time of Dissociation vs. Surrounding Temperature for Spheres of Limestone  
Initial temperature— $t_0 = 1600^\circ \text{F.}$  Curve numbers are diameters in inches

to the Gurney plots. This value becomes 0.0081 square foot per hour (Table II). The value of  $K$ , thermal conductivity, must be given a "dissociation" value to correspond with that found for  $\alpha_w^2$ . This value is 0.625 (B. t. u. per hour per square foot per ° F. per foot) and it must be used in computing the emissivity of limestone being dissociated into lime.

#### Use of the Plots

As regards practicability Figures 6 and 7 are important. With these plots it is possible to estimate the time necessary for complete dissociation of spheres under different conditions of preheat and with different surface temperatures.

*Example*—Estimate the time required to dissociate completely a block of lime whose shape may be assumed to be spherical.

Data:

Diameter	=	6 inches
Initial temperature	=	80° F.
Surrounding temperature	=	2100° F.

Solution: In Figure 6 the 2100° F. line intersects the 6-inch line at 1.5. Then  $\sqrt{\theta} = 1.5$

$$\text{or} \quad \theta = (1.5)^2 = 2.25 \text{ hours}$$

In the same way the time for dissociating spheres of other dimensions for the same and for different surface temperatures above 1700° F. can be determined. A series of curves showing time as a function of surface temperature for different sizes could then be plotted as in Figure 9.

Table II contains a list of constants for lime and limestone, together with units in which these constants are expressed. These data have been collected from various sources and are thought to be reasonably reliable.

Table II—Thermal and Physical Constants for Lime and Limestone

CONSTANT	UNITS	LIME	AUTHORITY	LIMESTONE	AUTHORITY
$\alpha^2 = \frac{K}{SC}$	Sq. ft./hr.	0.0188	<sup>a</sup>	0.045	<sup>a</sup>
$K$	B. t. u./hr./sq. ft./° F./ft.	0.4	Block	1.47	Tadokaro
$S$	Lbs./cu. ft.	92.6	<sup>a</sup> (assuming negligible contraction)	165	Tadokaro
$Q$	B. t. u./lb.			710 at 900° C.	Smyth and Adams
$C$	B. t. u./lb./° F.	0.23		0.198	Tadokaro
$l_D$				1650 <sup>b</sup>	Knibbs

<sup>a</sup> Calculated from other constants.  
<sup>b</sup> 1700° F. used in all calculations.

## Gases from Sewage Sludge Digestion<sup>1</sup>

W. D. Hatfield, G. E. Symons, and R. R. Mills

SANITARY DISTRICT OF DECATUR, ILL.

THE sewage from the city of Decatur, Ill., is a mixture of 5 million gallons of domestic sewage per day from a population of 40,000, including the normal industrial wastes from a city of that size, and 5 million gallons of waste from the Staley Corn Products Manufacturing Company. The mixture as received at the sewage plant is about five times as strong as a normal city sewage. The minimum temperature of the sewage in the winter is about 20° C. and the maximum in the summer is about 40° C. This combination of unusual strength and high sewage temperature has made the operation of the Decatur sewage plant of unusual interest.

Under these conditions rapid putrefaction takes place in the sewage system and treatment plant, thus making a considerable odor nuisance. The sewer gas, the Imhoff tank gas, and the air above all conduits and points of agitation are charged with hydrogen sulfide. The Imhoff tank gases<sup>2</sup> have been completely trapped and are used to burn up the odors which are now collected by a suction fan from the covered grit chamber and the covered conduits and by-passes. A slight odor of sulfur dioxide is noticeable near the oven for burning the gases, but it is not sufficient to cause complaint, even near by.

The relation of the temperature of the sludge digestion chamber to the hydrogen sulfide content and volume of the

The rate and volume of gas production from sludge digestion in Imhoff tanks and the hydrogen sulfide content of the gas are directly proportional to the temperature of digestion.

Experimental laboratory data are given showing the maximum gas rate at about 30° C. At higher temperatures the rate is less. At 30° to 35° C. from 40 to 50 per cent of the gas produced is from sludge added during the last 24 hours. The per cent of gas formed in the first 24 hours is given for lower temperatures.

The Decatur Imhoff tanks demonstrate on a large scale the advantage of heating sludge-digestion chambers to increase rate of digestion and increase the sludge capacity through rapid digestion. The chief components of the Imhoff gas are: methane 70, carbon dioxide 20, and nitrogen 7 per cent.

Imhoff tank gases is shown in Figures 1 and 2. High hydrogen sulfide content and large volumes of gas are coincident with high temperatures of sludge digestion.

During the time that these data were being collected on the large-scale experiments on the Imhoff tanks, considerable data were being accumulated in the laboratory, where conditions may be more carefully controlled than on plant operation. The unusually large volume of gas being produced by the tanks was of interest to all who visited the

Decatur plant. The relation of temperature and starch wastes was of particular interest because of a program of recovery of the starch waste undertaken by the Staley Company. Many preliminary tests were made by inoculating fresh sludge with digested sludge and incubating at different temperatures for various periods of time. Only the final set of experiments is reported here.

#### Experimental Procedure

The sludge was digested in a 2-liter, wide-mouth glass bottle fitted with a rubber stopper. Through the stopper were three glass tubes—a delivery tube for collecting the gas over water, a tube through which daily additions of sludge were made, and a siphon tube for drawing off supernatant liquor. These experiments were made to approximate conditions in the Imhoff tank and instead of seeding the fresh sludge with old sludge in the proportions of 4 to 1, as has often been done, about 250 cc. of well-digested Imhoff tank sludge (22 grams dry weight) were added to the 2-liter

<sup>1</sup> Presented before the Division of Water, Sewage, and Sanitation Chemistry at the 74th Meeting of the American Chemical Society, Detroit, Mich., September 5 to 10, 1927.

<sup>2</sup> Hatfield, *Public Works*, 58, 204 (1927).



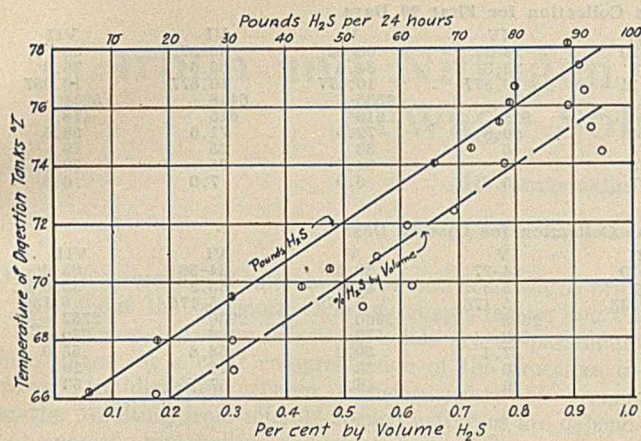


Figure 1

bottle and this was covered with 1500 cc. of supernatant liquor having a pH of 7.4. The bottles were then incubated for 4 days until gasification seemed negligible.

Daily sludge additions were made with fresh sludge collected by settling 10 gallons of sewage for 1 hour. The volume of sludge added was from 5 to 10 ml. per day and the amount of organic matter from 0.1 to 0.2 gram per day. There were approximately 9 grams of organic matter in the digested sludge in the bottles, thus making the proportion of 1 part of fresh organic matter to 90 parts of old organic matter. This proportion was satisfactory according to a recent publication by Rudolfs,<sup>3</sup> but at the time of our experiments it was taken as approximating our Imhoff tank conditions. The same amount of supernatant liquor was siphoned off each day as fresh sludge was added, thus keeping the water level the same and preventing the end products of digestion from accumulating and hindering the normal biological digestion. The bottles were shaken once each day.

In this set of experiments seven bottles were used. Nos. III, IV, V, VI, and VII were each incubated at almost constant temperatures. No. I was held at 20° C. for 27 days and then was changed to 10–12° C. No. II was started at 11° C. and gradually increased to 20° C. during the 130 days of the experiment. No. III remained at 20° C. throughout the experiments. No. VII differs from the rest in that

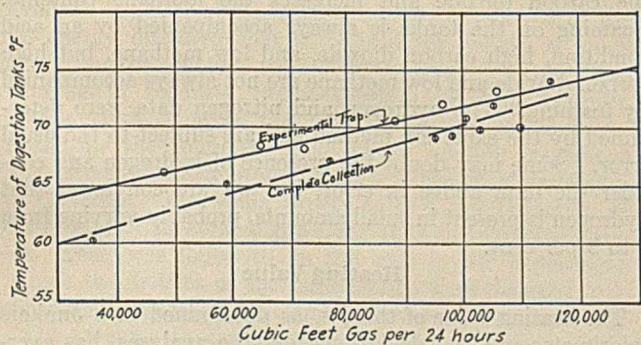


Figure 2

no digested sludge was used for inoculation, but daily additions of sludge were started in a bottle of clear supernatant liquor. No. VII was incubated at 36° C. Data on Nos. II and VII are not comparable with the others because conditions were decidedly different. However, the information obtained from them is valuable and they have therefore been included.

The daily data on No. II show that the rate of gas production at 20° C. is greatly accelerated by allowing the sludge

<sup>3</sup> New Jersey Agr. Expt. Sta., Report of Sewage Substation, 1926.

to accumulate at lower temperatures. The total gas produced in 90 or 130 days was greater than that produced by Nos. III or IV. This must have been due to certain liquefaction at low temperatures which made the organic matter more susceptible to gasification when the temperature was raised. The data on No. VII show that at high temperatures sludge digestion very rapidly becomes normal even without initial inoculation. A question which is not answered is—Is the lower rate and total gas production after 50 days of No. VII due to the absence of organic matter in the inoculation sludge used in the other bottles or to lack of proper inoculation?

Table I contains the data on the first 90 days after sludge additions were started. Figure 3 shows the total volumes of gas produced in 90 and 130 days. All sludge additions were stopped on the 97th day. Figure 5 gives the average volume of gas formed during each 10-day period per gram of organic matter added. Curves V and VI (Figure 5) show that during the first 30 days at 30° to 35° C. large quantities of gas were given off by the inoculating sludge. In curves I, III, and IV, 30 days were required for the processes of digestion to come to equilibrium. All the curves after the 40th day become a relatively straight line. For this reason

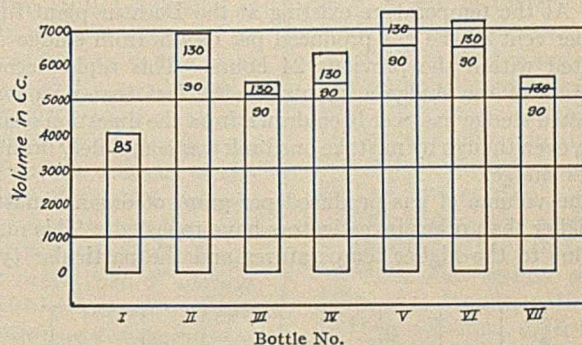


Figure 3—Total Volume of Gas Produced in 90 Days

40 days are considered necessary for the establishment of equilibrium conditions and therefore the true gas rate is best indicated by discarding the first 40 days and studying the rate thereafter. In this experiment from the 40th to the 90th day has been chosen as giving the most reliable data. These data are shown in Table II and Figure 4, as well as part of Figure 5.

The data presented in these tables may be summarized as follows:

- (1) Temperature has a direct influence on the rate of gas formation, which increases as the temperature approaches 30–33° C. and then decreases as 35° C. is reached.
- (2) Sludges accumulated during cool temperatures apparently break down into compounds which later at higher temperatures give a greater rate and volume of gas than sludges held at somewhat higher but constant temperatures during digestion.
- (3) The total volume of gas obtained in normal tank operation is proportional to the temperature and rate of gas production, even though the total gas production may eventually be the same at all temperatures, because the sludge is drawn before gas production is complete. Sludge seldom remains in the Decatur tanks more than 90 days and averages less than that.
- (4) The temperature affects the acidity of the digestion chamber under the conditions of the Decatur sewage. The reaction in the Imhoff tanks is 6.8 to 7.0 pH.
- (5) The rapidity of gas formation is discussed below.

#### Rapidity of Gas Formation

An interesting feature at the Decatur plant is the great reduction in gas production only a few hours after the Staley Starch Company has shut down. This immediate effect

Table I—Experimental Data on Gas Collection for First 90 Days

Series	I	II	III	IV	V	VI	VII
Temperature, ° C.	20-11	11-20	18-20	23-27	30-32	35-37	35-37
Average, ° C.	13.3	16.3	18.8	25.3	31.6	35.6	36.3
Organic matter, grams	10.14	10.577	10.14	10.577	10.577	10.577	10.987
Total gas, ml.	4007	5921	5163	5470	6535	6448	5261
Ml. gas per gram organic matter	395	560	510	518	618	615	478
Av. ml. gas per day	47.1	65.8	57.4	60.8	72.5	71.6	58.5
Ml. per day, no sludge added	33	54	37	40	33	25	29
Per cent reduction in 24 hours	30	18	35.5	34	54.5	65	50.3
pH	6.6	6.6	6.7	6.8	6.9	7.0	6.8

Table II—Experimental Data on Gas Collection for Last 50 Days

Series	I	II	III	IV	V	VI	VII
Temperature, ° C.	10-12	16-19	18-19	24-27	30-33	34-36	35-36
Average, ° C.	11.45	17.5	18.7	25.3	31.4	35.2	35.6
Organic matter, grams	4.249	5.176	4.333	5.176	5.176	5.176	5.130
Total gas, ml.	1697	3671	2162	2858	2960	2930	2752
Ml. gas per gram organic matter	400	710	500	552	572	566	530
Av. ml. gas per day	34	74.5	43	57.1	59.2	58.6	55.0
Ml. per day, no sludge added	33	54	37	40	33	25	29
Per cent reduction in 24 hours	3	27.5	14	30	46	57	53

could be due only to the drop in temperature of the tanks, which is slow, and the lack of food supply in sludge from the starch works. To test this out, occasionally the sludge additions to the bottles were omitted for one day and then resumed as usual. The average volume of gas produced during the 24 hours following after the omission of the sludge addition, and the percentage reduction of volume below that regularly obtained are shown in the last two lines of Table II. At the temperature existing at the Decatur plant fully 50 per cent of the gas produced per day is from sludge deposited within the previous 24 hours. This rapid decomposition of the sludge accounts for the fact that no poorly digested sludge has ever been drawn from the digestion chambers, even though by mistake one tank was completely drained of its sludge.

The volume of gas produced per gram of organic matter is higher than other investigators have reported. This must be due to the higher temperatures and the particular type

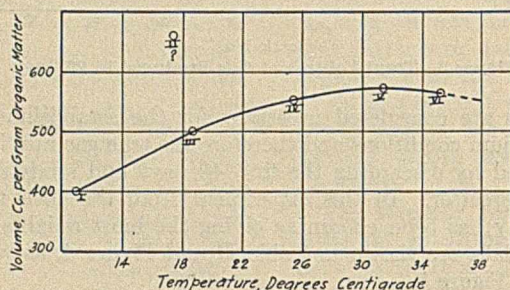


Figure 4—Temperature-Volume Relation during Last 50 Days of Sludge Additions

of organic matter settling from the starch waste-sewage mixture. The organic matter in the starch wastes is chiefly soluble matter from the corn and contains very little, if any, starch, gluten, or sugar.

#### Acidity

The acidity of the sewage is about 6.5 pH. Table I gives the pH values of the supernatant liquor in each bottle after the first 40 days. Under the conditions in Decatur satisfactory digestion takes place at a pH of 6.8 to 7.0, foaming conditions being accompanied by a pH of 6.5.

Routine analyses of the gas collected from the Imhoff tanks have been made since October, 1926, and are summarized as follows:

GAS	MINIMUM	MAXIMUM	AVERAGE	FOAMING TANKS
	Per cent	Per cent	Per cent	
Methane	55	74	68	60-64
Carbon dioxide	16	34	22	30-33
Hydrogen (?)	0	4	2	2
Nitrogen	4	10	6	7
Oxygen	0	0	0	0

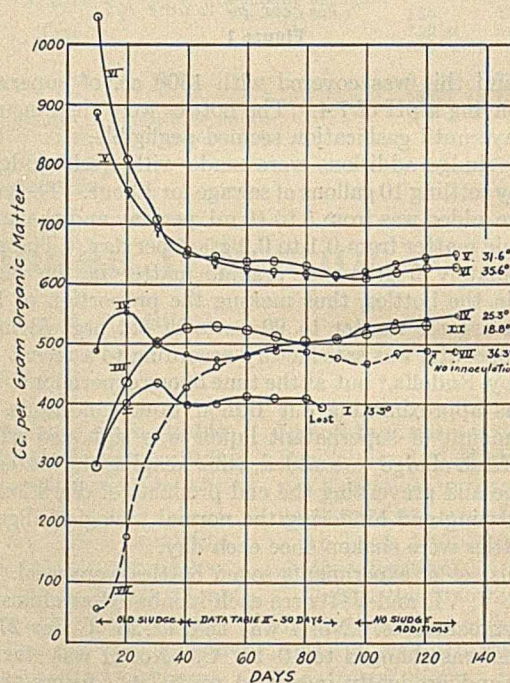


Figure 5—Rate of Gas Formation for 10-Day Period

A shutdown at the starch factory invariably decreases the carbon dioxide and increases the methane contents. Foaming in the tanks is always accompanied by an acid condition, high carbon dioxide, and low methane, but high carbon dioxide and low methane are not always accompanied by foaming. The hydrogen and nitrogen data were determined by the explosion method and are subject to the usual error. Some may doubt the presence of hydrogen and consider the data above in error, but we are convinced that hydrogen is present in small amounts, probably varying from 1 to 3 per cent.

#### Heating Value

The heating value of the gas, as determined in a Junkers calorimeter and by calculation from the analyses, has averaged about 700 B. t. u. per cubic foot. The gas is being used to destroy odorous gases, to heat the various buildings, and to heat the air for the activated sludge plant before compression.

Reports from the Department of Commerce are that the amalgamation efforts of the Heyl-Beringen A. G. have gone far beyond their original goal. It has extended its raw-material basis by working with Gebruder Gutsbrod G., m. b. H., of Frankfurt, and now wishes to bring about an amalgamation of the principal German mineral-color producers with the intention of later founding a Deutschen Farbwerke A. G. with a capital of 15,000,000 to 20,000,000 reichsmarks.

# Carbon and Nitrogen Transformation in Fresh Sewage Solids Digestion<sup>1,2</sup>

H. Heukelekian and Willem Rudolfs

AGRICULTURAL EXPERIMENT STATION, NEW BRUNSWICK, N. J.

THE principles of microbiological activities which bring about the transformation of organic matter and the final stabilization of sewage solids are of paramount importance for a clear comprehension of the processes involved in digestion. These transformations of organic matter resulting from microbiological activities are dependent upon the metabolism and physiology of the organisms. Those transformations which involve carbon and nitrogen, the foundation materials of the cell protoplasm, are the most vital. The physico-chemical character of the organic matter containing these elements largely determines the type and degree of decomposition.

The microorganisms attack the carbon to obtain energy necessary for their life activities and for synthesis of their protoplasm. A certain amount of energy is also required for growth and multiplication of the cells. The proportion of the total energy liberated that is utilized for growth is determined (1) by the environmental conditions, (2) by the nature of the organisms, (3) by the source of the energy material, and (4) by the degree of the transformation.

Variation in the air supply is an example of the first of these conditions. Under aerobic conditions such as prevail in the activated-sludge process, the amount of the total energy liberated that is utilized for growth is much higher than the amount utilized under anaerobic conditions prevailing in separate sludge-digestion or Imhoff tanks. In other words, more of the material decomposed is resynthesized in the microbial cells under aerobic conditions of the activated-sludge process than is in the anaerobic digestion processes. We would expect to find less reduction of volatile matter in aerobic processes than in anaerobic processes. Such was found to be the case in an experiment in which two bottles of the same sludge were digested, one under strictly anaerobic conditions and the other occasionally allowed to come in contact with air.

The environmental conditions also determine the degree of the transformation of the energy material and the amount of energy liberated. Under aerobic conditions the digestion goes to completion with the liberation of end products such as carbon dioxide, water vapor, and ammonia, which contain but little energy for microorganisms. Under anaerobic conditions various intermediate products are formed which contain energy that may be utilized further for synthesis.

Unlike carbon, nitrogen is utilized by the organisms only for synthetic purposes. Microbial cells contain 5 to 15 per cent nitrogen, which must be supplied either by proteins or by their degradation products before growth can take place.

When carbohydrates are used for energy the organisms must obtain their nitrogen from another source, either inorganic or organic. Ammonia is left as a waste product only after the nitrogen required by these organisms for synthesis is satisfied.

After this brief discussion of carbon and nitrogen transfor-

mations, as affected by the metabolism of the organisms, it will be understood that these transformations are vital to the life and activities of the organisms and that fundamental changes are brought about in their activities by such factors as air and food supply.

This study was undertaken with the hope that by following the carbon and nitrogen transformations during digestion of fresh sewage sludge it might be possible to derive some fundamental principles directing the course and nature of digestion. It was also hoped that some light might be thrown on the differences in the course of di-

gestion of limed and unlimed material. It has been demonstrated as a result of studies in this laboratory that judicious application of lime accelerates the rate of digestion and increases the rate of gas production. Consequently, the question presents itself as to the nature of substances that are decomposed as a result of lime addition. That the addition of lime unlocks certain substances the decomposition of which gives great volumes of gas has not been realized before.

## Method

Equal amounts of fresh solids from the Plainfield plant were put into two bottles. To one bottle lime was added to maintain a pH of 7.4. The material was incubated at 24° C. Frequent determinations were made of pH value, solids, ash, and Kjeldahl nitrogen. Organic carbon was determined by the wet combustion method after driving off the dissolved carbon dioxide and the carbonates by bringing to a boil in acid solution.

Mention must be made here of the irregularities in sampling caused by the growth of fungus, especially on the surface of the unlimed material. Some of the apparent inconsistencies in the curves were caused by uneven distribution of the fungus mat.

The carbon and nitrogen changes in the digestion of limed and unlimed fresh solids have been followed. It has been found that there is no reduction in the total nitrogen content in a given volume of digesting sludge. The percentage nitrogen of the volatile matter, on the other hand, increases as a result of the reduction in volatile matter. The increase of carbon content of the volatile matter and the reduction of volatile matter, in the unlimed material, just balance each other. In limed material there is a greater reduction of volatile matter and carbon. The most rapid rate of carbon reduction takes place after the cellulose-decomposition stage, and it is suggested that cellulose decomposition products, as well as the decomposition of another carbonaceous material—namely, the fats—cause this rapid reduction of carbon. It is pointed out that a greater proportion of the organic matter decomposed is gasified as a result of liming.

<sup>1</sup> Presented by Mr. Rudolfs before the Division of Water, Sewage, and Sanitation Chemistry at the 74th Meeting of the American Chemical Society, Detroit, Mich., September 5 to 10, 1927.

<sup>2</sup> Paper No. 55, Department of Sewage Disposal, New Jersey Agricultural Experiment Station, New Brunswick, N. J.

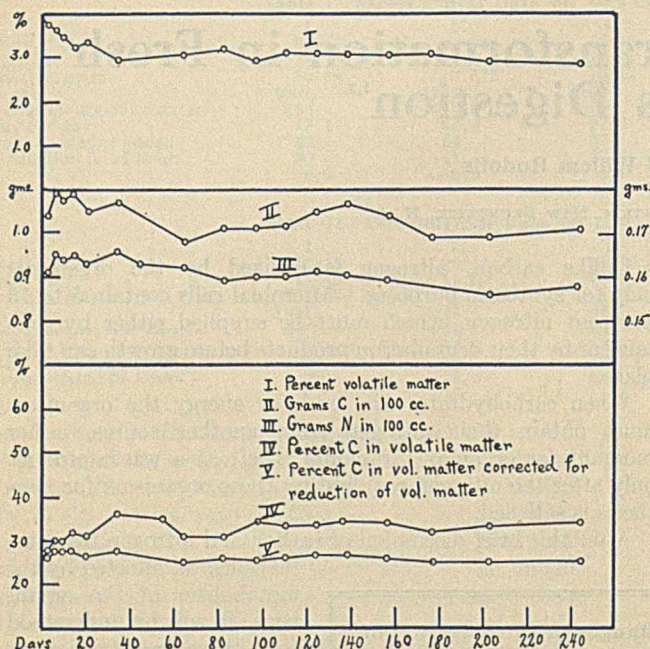


Figure 1—Volatile Matter, Carbon, and Nitrogen in Unlimed Digesting Sewage Solids

### Results

The results are presented graphically in Figures 1 and 2.

**UNLIMED MATERIAL**—The digestion of unlimed fresh solids was very slow, as indicated by the curve of volatile-matter content<sup>3</sup> (Figure 1, curve I). During the 8 months of digestion the volatile matter was reduced only 25 per cent. The amount of carbon present in 100 cc. of this material at different dates showed some fluctuation with a very slow reduction amounting to about 5 per cent (curve II). But at the end this reduced amount of carbon was contained in a smaller amount of volatile matter and hence the percentage of carbon in the volatile matter was high (curve IV). With a 25 per cent reduction of volatile matter there was about 30 per cent increase in carbon content of the volatile matter. In other words, the increase in carbon paralleled the decrease of volatile matter and the original relationship of the organic matter to its carbon content was not altered. When, therefore, the reduction of volatile matter is compared on the basis of the original volatile matter content of the material, the percentage of carbon in the volatile matter is proved to be constant (curve V). The results for curve V are obtained in the following way:

$$\frac{-a_n \times b_n}{c}$$

where  $a$  = per cent volatile matter at  $n$  date  
 $b$  = per cent carbon in volatile matter at  $n$  date  
 $c$  = per cent volatile matter at beginning

The nitrogen content of this material showed a slight initial increase followed by slow and gradual decrease (curve III).

**LIMED MATERIAL**—When lime was added to the fresh solids to maintain the pH value at 7.4 the digestion of the material was hastened, so that there was about 60 per cent reduction of volatile matter within 3 months (Figure 2, curve I, results corrected for the lime added). The amount of carbon present in this material decreased rapidly after the first 60 days, until at the end a 30 per cent reduction was evident (curve II). After the volatile-matter reduction had ceased there was a steady decrease in the carbon content.

<sup>3</sup> Volatile matter as given in the test is equivalent to "loss on ignition."

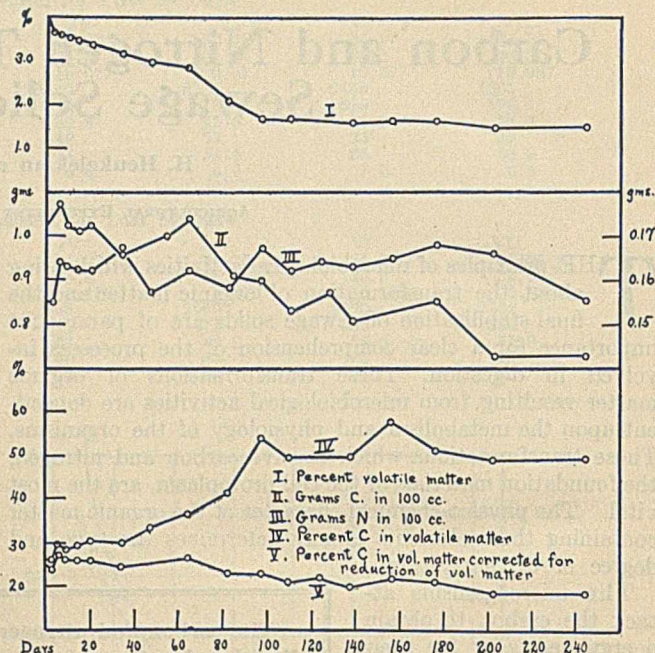


Figure 2—Volatile Matter, Carbon, and Nitrogen in Limed Digesting Sewage Solids

The percentage of carbon in the volatile matter increased steadily from 26 to 50 per cent during the first 100 days of the incubation, after which it became more or less constant (curve IV). The apparent percentage increase is due to the reduction of part of the volatile matter and not to an actual addition of carbon. When compared on the basis of the initial volatile matter, there is obviously a decrease in the percentage carbon content of the volatile matter (curve V). Assuming the original volatile-matter content as 100 with 26 per cent carbon, we find at the end only 40 parts volatile matter with a carbon content of 50 per cent.

The nitrogen content of the limed material showed an initial increase, followed first by a drop and then by a second increase (curve III). It must be borne in mind that this is the total amount of nitrogen present in 100 cc. of the material. The nitrogen content, on the basis of volatile matter, naturally increased, since with a constant nitrogen content volatile matter was decreasing rapidly.

### Discussion

**NITROGEN TRANSFORMATION**—To take up first the changes in the nitrogen content, it will be seen that if the figures are significant there is an absolute increase in the amount of nitrogen as a result of digestion. It is true that the differences are small and too much emphasis should not be laid on it; yet in view of the fact that the total-nitrogen determination is quite accurate and the results are persistent, an explanation may be offered. The fixation of nitrogen under anaerobic conditions in the presence of abundant and suitable carbon supply is entirely feasible. At any rate, the digestion did not bring about a reduction in the nitrogen content of either the limed or unlimed materials. It is true that a certain amount of nitrogen is lost in the gas, but this does not seem to be appreciable (usually from 3 to 8 per cent). Thus digestion brought about a change in the form rather than in the quantity of nitrogen. On the other hand, on the basis of volatile matter there is an actual increase in the nitrogen content. Thus, if we start with 100 grams of volatile matter in the fresh solids with a 4.0 per cent nitrogen content, as a result of digestion the volatile

matter will be reduced to 50 grams but the nitrogen in the remaining volatile matter will be 8.0 per cent.

**CARBON TRANSFORMATION**—The reduction of carbon in the unlimed material parallels the reduction of volatile matter. In both cases the reduction is lower with unlimed than with the limed material. The addition of lime stimulates the decomposition of organic matter, especially the carbonaceous constituents. The most rapid reduction in the carbon content takes place in the later stages of decomposition. The decomposition of cellulose, which takes place in the early stages of digestion, is not accompanied by a material reduction in the carbon content because, in the first place, cellulose constitutes only 5 to 10 per cent of the dry material of the fresh solids, and second, the decomposition products of cellulose, the organic acids, are broken down in the later stages of digestion. Undoubtedly, the decomposition of some carbonaceous substance besides cellulose is the cause of this rapid decrease in the carbon content. It is suggested that the addition of lime accelerates the decomposition of fats, thus causing a great reduction of carbon and volatile matter. Decomposition of fats takes place only in the later stages of digestion.

In the case of unlimed material a 25 per cent reduction of volatile matter was accompanied by only 5 per cent

reduction of carbon, while in the limed material a 60 per cent reduction of volatile matter was accompanied by a 30 per cent reduction in the carbon content. It would therefore appear that not only does the addition of lime cause a greater reduction of volatile matter, but also a greater proportion of this volatile matter is gasified, whereas in the unlimed material a greater proportion of the decomposed material is left in intermediate forms—that is, liquefied. Thus, it would seem that the addition of lime not only brings into the range of decomposition a greater proportion of substances, but also causes the decomposition of these substances to give greater volumes of gas. Lime causes a more rapid and also a more complete decomposition of the substances that would either decompose partially or not at all.

The increase in the carbon content of the volatile matter is not an actual increase, but only an apparent one due to the reduction of the volatile matter. When this is remembered the percentage content of carbon is seen to be actually decreasing in the limed material. On the other hand, the volatile matter of the sludge obtained at the end of the decomposition has a higher percentage of carbon. The explanation is obvious since the process of humification is one of enrichment of carbon; the higher the degree of humification the greater the percentage of carbon.

## Effect of Addition of Salts on the Germicidal Efficiency of Sodium Hydroxide<sup>1</sup>

Max Levine, J. H. Toulouse, and J. H. Buchanan

DEPARTMENTS OF CHEMISTRY AND BACTERIOLOGY, IOWA STATE COLLEGE, AMES, IA.

IN A previous paper<sup>2</sup> it was shown that with the same sodium hydroxide concentration the addition of sodium carbonate increased the efficiency of the germicidal action of the solution. In this paper are given the results of adding salts, with particular reference to sodium chloride.

The details of preparation of the culture and technic of disinfection were identical with that previously described.<sup>3</sup> The time required to effect a reduction of 99.9 per cent of the exposed bacteria was employed as a basis for comparison.

Preliminary experiments showed the following:

(1) 1.16 per cent NaCl, 1.5 per cent KCl, and 1.07 per cent Na<sub>2</sub>CO<sub>3</sub> decreased the killing time of 0.5 *N* NaOH at 50° C. when the salts were added to the alkali.

(2) NaCl, KCl, Na<sub>2</sub>CO<sub>3</sub>, and Na<sub>3</sub>PO<sub>4</sub>·12H<sub>2</sub>O were only weakly germicidal for the test organisms, showing reduction of less than 30 per cent in 1 hour at 60° C.

### Experimental

**EXPERIMENTS AT 50° C.**—To 100 cc. of 0.5 *N* sodium hydroxide in a three-necked Woulfe bottle was added the desired amount of sodium chloride or carbonate (dry salt). The mixture was sterilized in the autoclave at 15 pounds (1 atmosphere) for 20 minutes. After cooling, the contents of the bottle were brought to the desired temperature in a water bath, inoculated with the test organism, and the surviving bacteria determined as previously described. The results are summarized in Table I.

Figures 1 and 2 show curves obtained by plotting logarithms of the average per cent surviving bacteria against time.

Table I—Effect of Concentration of Added Salts on Killing Time of 0.5 *N* Sodium Hydroxide at 50° C.

ADDED SALT Per cent	KILLING TIME 99.9 PER CENT OF EXPOSED BACTERIA	
	NaCl Minutes	Na <sub>2</sub> CO <sub>3</sub> Minutes
0	41.0	41.0
1	34.4	33.8
2	29.9	29.9
3	25.2	25.5

It will be observed from Table I that the addition of sodium chloride or sodium carbonate decreased the killing time of sodium hydroxide and that the decrease was proportional to the quantities of added salts. Sodium chloride and sodium carbonate were equally effective in this respect. The killing time was effectively reduced 16.8, 27.00, and 38.3 per cent by the addition of 1.0, 2.0, and 3.0 per cent of the salts, respectively. There was no significant change in the H-ion concentration due to the addition of these salts.

Table II—Effect of Concentration of Added Salts on Killing Time of 0.25 *N* Sodium Hydroxide at 60° C.

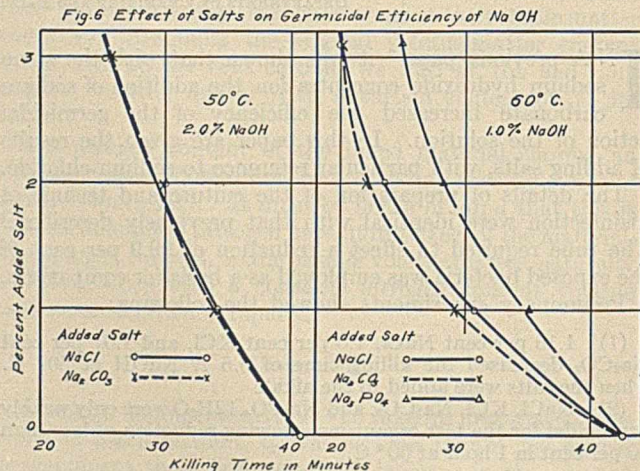
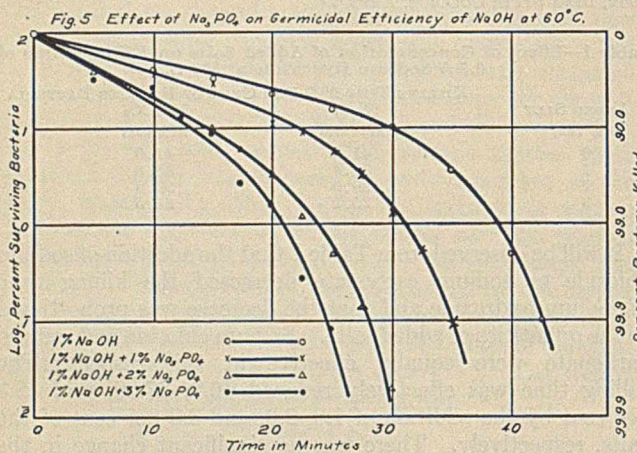
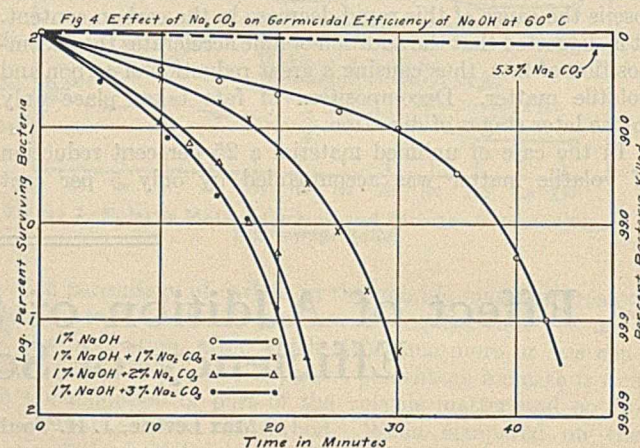
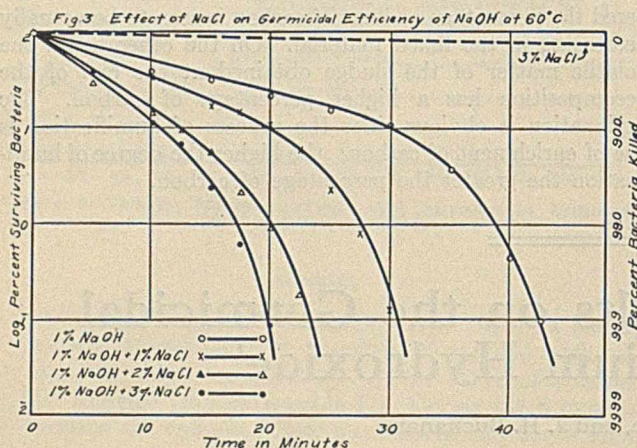
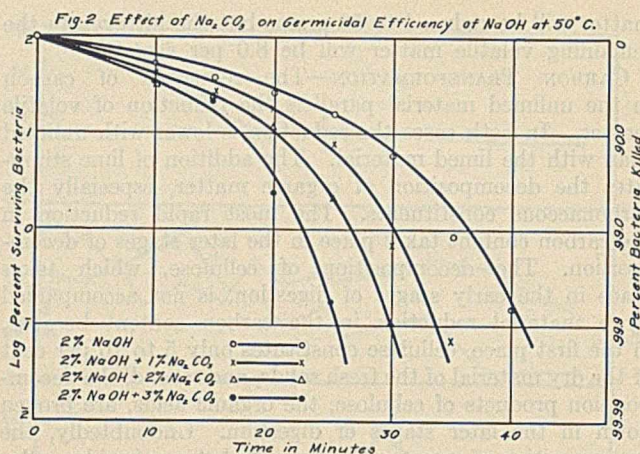
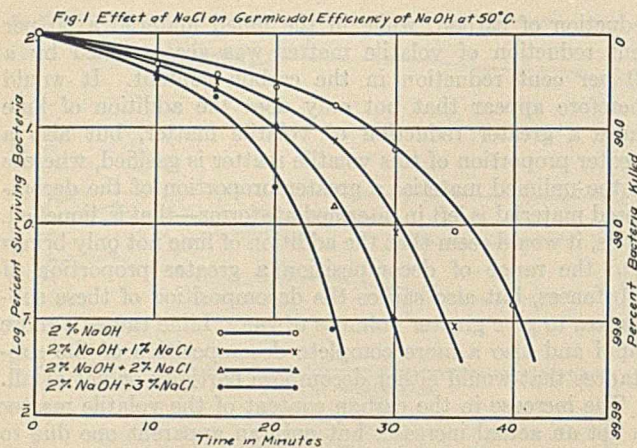
ADDED SALT Per cent	KILLING TIME 99.9 PER CENT OF EXPOSED BACTERIA		
	NaCl Minutes	Na <sub>2</sub> CO <sub>3</sub> Minutes	Na <sub>3</sub> PO <sub>4</sub> ·12H <sub>2</sub> O Minutes
0	42.5	42.5	42.5
1	30.6	29.0	34.9
2	23.4	21.9	28.1
3	19.9	20.1	24.7

**EXPERIMENTS AT 60° C.**—Owing to the greater sterilizing effect at 60° C., a sodium hydroxide solution 0.25 *N* was used in place of the 0.5 *N* solution employed at 50° C. Sodium chloride, sodium carbonate, and trisodium phosphate were the salts used, in strengths of 1.0, 2.0, and 3.0 per cent, respectively. The increased sterilizing efficiency of the sodium hydroxide with the addition of these salts is given in Table II and in Figures 3, 4, and 5.

<sup>1</sup> Received September 17, 1927. This study was made possible through a fellowship maintained by the American Bottlers of Carbonated Beverages at Iowa State College.

<sup>2</sup> *Ind. Eng. Chem.*, 20, 63 (1928).

<sup>3</sup> *Iowa State College J. Science*, 1, No. 4, 379 (1927).



Here again it is evident that all three salts distinctly decreased the killing times. The influence of the sodium chloride and sodium carbonate was approximately the same while the phosphate was less efficient. Thus with the addition of 1.0 per cent of the salts a reduction of 28, 30, and 17 per cent, respectively, was obtained in the time required to effect a reduction of 99.9 per cent of the exposed bacteria. These observations were made on the basis of equal quantities, by weight, of the salts. If equivalent quantities of chloride, carbonate, and phosphate had been added on the basis of the sodium ion, the phosphate would have been more effective with respect to a reduction in the killing time.

#### Discussion

No adequate explanation of the influence of the added salts is yet demonstrable. It is conceivable that the un-

dissociated sodium hydroxide rather than the OH ion may be the agent which penetrates the bacterial cell, thereby causing death of the organism. Addition of the various salts employed would tend to decrease the dissociation of sodium hydroxide and thus increase the concentration of undissociated sodium hydroxide, resulting in an increased germicidal efficiency.

Another explanation is that the added salts would decrease the solubility of the sodium hydroxide in the water phase of the bacterial suspension, and as a consequence the sodium hydroxide would be forced into the bacterial phase. Work is in progress at the present time to determine this point.

The results shown in Figure 6 enable one to calculate the relative effects of addition of sodium chloride, sodium carbonate, and sodium phosphate to a solution of sodium hydroxide, on the germicidal efficiency of the NaOH.

### Summary

The addition of sodium chloride, sodium carbonate, or trisodium phosphate to sodium hydroxide markedly decreases the killing time at 50° and 60° C.

The effects of equal weights of sodium chloride and sodium carbonate are approximately the same, whereas the trisodium phosphate is less efficient.

As the concentration of salts added to the sodium hy-

droxide is increased the killing time is decreased, but at a decreasing rate.

It is suggested that the undissociated sodium hydroxide may be the agent which penetrates the cell. The addition of the various salts would increase the concentration of undissociated sodium hydroxide, or possibly decrease the solubility of the sodium hydroxide in the water phase which would tend to force the sodium hydroxide into the bacterial phase of the suspension. In either case the effect would be to increase the death rate of the bacteria.

## Some Preliminary Experiments on Fat-Liquoring<sup>1</sup>

Henry B. Merrill

A. F. GALLUN & SONS CO., MILWAUKEE, WIS.

AT SOME stage between tanning and finishing all leather undergoes a treatment designed to incorporate in the tanned skin a certain amount of oil. Light leathers are generally drummed with an emulsion of various animal or vegetable oils, the process being known as "fat-liquoring." If the operation is properly carried out, nearly all the oil in the fat-liquor is absorbed by the skins, the used liquor is nearly clear, and the skins themselves neither look nor feel greasy, in spite of containing up to 20 per cent of fats and oils.

Almost no quantitative work has been done on the chemistry of fat-liquoring. Except that it has been recognized that a fat-liquor must be a fairly stable emulsion, almost nothing is known of the nature of the interaction of oil and leather, and of the variables which affect it. Most of the fat-liquors in use are quite complex, containing numerous constituents in proportions which are juggled until a desired effect is obtained, after which the formula thus obtained is adhered to rigidly.

Preliminary to any attempt to determine the function and laws governing the employment of the various constituents of practical fat-liquors, it is necessary to study in

### Experimental Procedure

The fat-liquors employed contained nothing but water and a sulfonated neat's-foot oil (H<sub>2</sub>O, 22.3; ash, 4.7; total oil, 73.0; SO<sub>3</sub> combined with oil, 3.4 per cent), plus borax or sodium carbonate to regulate the pH value. The leather employed was ordinary 1-bath chrome calf, taken after coloring but before fat-liquoring. Small strips of this leather were fat-liquored under controlled conditions and, after drying, were split into five layers on a skiving machine. Each split was analyzed for fat, and from the thickness of the several splits and their fat content the penetration of the oil into the skin was shown, as well as the total amount of oil taken up by the leather as a whole. The exact composition of the liquors and the time of fat-liquoring are given in connection with the figures. In all cases the temperature was 40° C. at the outset, and fell off but little during the course of the experiment. In expressing the results obtained for distribution of oil in the skin, the percentage of fat (dry basis) in each layer was plotted as a function of the depth of the center of that layer below the grain surface in percentage of the total thickness of the skin.

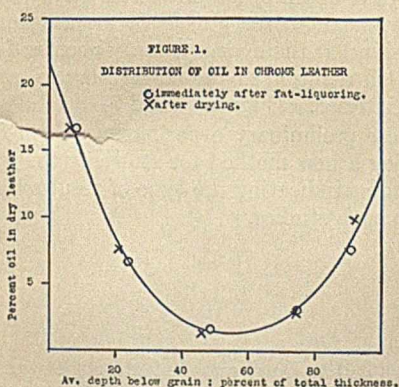


FIGURE 1.  
DISTRIBUTION OF OIL IN CHROME LEATHER  
○ Immediately after fat-liquoring.  
× After drying.  
Fat-liquor: 2.5 grams sulfonated neat's-foot oil; 0.25 gram borax in 50 cc. per 100 grams wet leather. Time: 2 hours

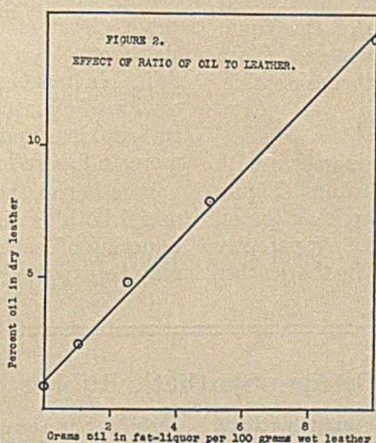


FIGURE 2.  
EFFECT OF RATIO OF OIL TO LEATHER.  
Fat-liquor: sulfonated neat's-foot oil and borax (10:1) in 50 cc. volume per 100 grams leather. Time: 2 hours

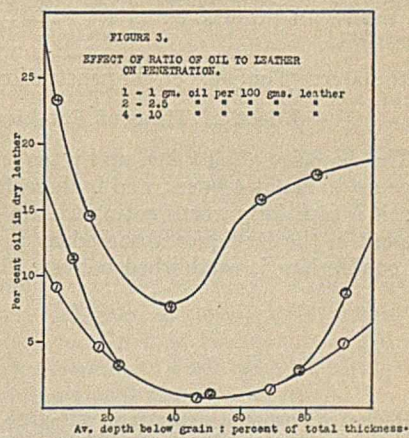


FIGURE 3.  
EFFECT OF RATIO OF OIL TO LEATHER ON PENETRATION.  
1 - 1 gm. oil per 100 gm. leather  
2 - 2.5 gm. oil per 100 gm. leather  
4 - 10 gm. oil per 100 gm. leather  
Fat-liquor: sulfonated neat's-foot oil and borax (10:1) in 50 cc. volume per 100 grams leather. Time: 2 hours.

the simplest possible system, the effect of such fundamental variables as ratio of oil to leather, concentration, time, and pH value upon the total quantity of oil absorbed and its distribution in the leather. The results of such experiments are reported in this paper.

<sup>1</sup> Presented under the title "A Preliminary Study of Fat-Liquoring" before the Division of Leather and Gelatin Chemistry at the 74th Meeting of the American Chemical Society, Detroit, Mich., September 5 to 10, 1927.

### Distribution of Oil—Effect of Drying

As will be seen from Figure 1, the distribution of fat in chrome leather is far from uniform. The center contains no oil except the natural skin fat. Contrary to a widespread impression, penetration of the oil does not take place chiefly through the flesh side; if anything, more oil is absorbed through the grain. No change occurs in the distribution of

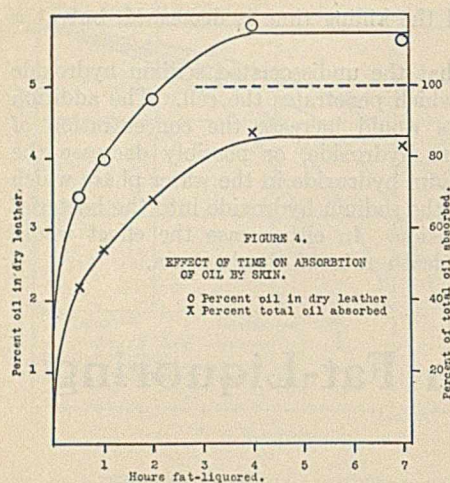


FIGURE 4.  
EFFECT OF TIME ON ABSORPTION OF OIL BY SKIN.  
O Percent oil in dry leather  
X Percent total oil absorbed

Fat-liquor: 2.5 grams sulfonated neat's-foot oil; 0.25 gram borax in 50 cc. per 100 grams wet leather

the fat when the leather is dried out or, indeed, at any subsequent time. Effect of Ratio of Oil to Leather

When the ratio of oil to leather is increased, the volume of the liquor being kept constant, the quantity of oil absorbed increases in direct proportion to the quantity present in the fat-liquor, as is shown by Figure 2. The fraction of the total oil that is absorbed thus remains constant; in these experiments approximately two-thirds of the oil was taken up in every case. Figure 3 shows that as the ratio of oil to leather is increased the first effect is to increase the oil content of the surface layers of the leather. Only when the ratio becomes very large does penetration into the center of the skin take place.

#### Effect of Concentration of Oil

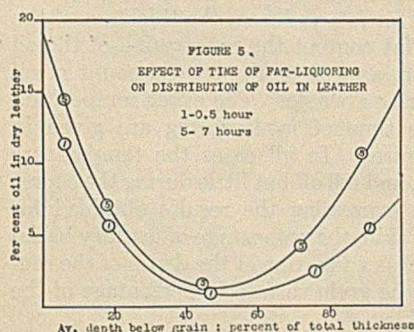


FIGURE 5.  
EFFECT OF TIME OF FAT-LIQUORING ON DISTRIBUTION OF OIL IN LEATHER  
1-0.5 hour  
5-7 hours

Fat-liquor: 2.5 grams sulfonated neat's-foot oil; 0.25 gram borax in 50 cc. per 100 grams wet leather

50 to 200 cc. The effect on the penetration was inconsiderable.

#### Effect of Time of Fat-Liquoring

The quantity of oil taken up by the leather increases with time up to about 4 hours, and is thereafter constant (Figure 4); it is especially worth noting that in no case is all the oil present in the fat-liquor absorbed by the skin. Apparently an equilibrium is established between the oil in the leather

and that remaining in the liquor. The additional quantity of oil taken up, as the time of fat-liquoring is increased from 0.5 to 4 hours, is fixed chiefly in the grain and flesh layers. (Figure 5) Penetration into the heart of the skin is but little increased by lengthening the time of fat-liquoring.

#### Effect of pH Value

Two sets of experiments were performed to determine the effect of hydrogen-ion concentration on the absorption and distribution of oil in leather. In the first, leather samples of the same pH value were fat-liquored with liquors containing increasing amounts of sodium carbonate so that the final pH values of the liquors varied from 5.1 to 8.1. In the second, strips of leather were brought to equilibrium with buffer solutions of pH values from 3 to 9, and were then fat-liquored with liquors all of which had the same pH value.

Rather unexpectedly it was found that shifting the pH value, either of the liquor or of the leather, had no appreciable effect on the total quantity of oil taken up by the skin. Increasing pH value, however, greatly favors the penetration of oil into the skin; as the hydroxyl-ion concentration goes up, less and less oil is found in the surface layers, and more and more in the interior. (Figures 6 and 7)

It is hoped that these preliminary experiments will prove useful both as disclosing a new method for studying the fat-liquoring of leather and as indicating the type of results that may be expected from such studies.

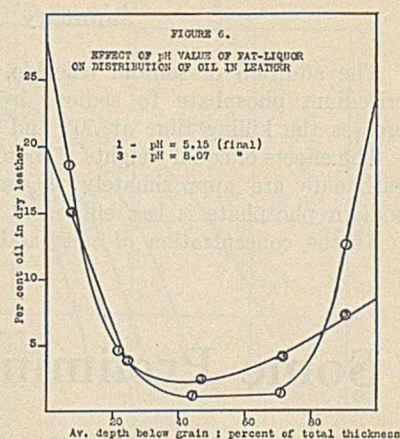


FIGURE 6.  
EFFECT OF pH VALUE OF FAT-LIQUOR ON DISTRIBUTION OF OIL IN LEATHER  
1 - pH = 5.15 (final)  
3 - pH = 8.07 "

Fat-liquor: 2.5 grams sulfonated neat's-foot oil X grams  $\text{Na}_2\text{CO}_3$  in 50 cc. per 100 grams wet leather. Time: 2 hours

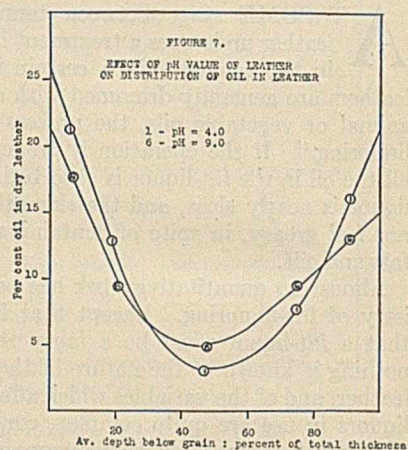


FIGURE 7.  
EFFECT OF pH VALUE OF LEATHER ON DISTRIBUTION OF OIL IN LEATHER  
1 - pH = 4.0  
6 - pH = 9.0

Fat-liquor: 4.0 grams sulfonated neat's-foot oil; 0.4 gram borax in 100 cc. per 100 grams wet leather. Time: 2 hours

## German Synthetic Rubber

Recent widespread newspaper publicity on German synthetic rubber was the result of an address made by Geheimrat von Weinberg of the German Dye Trust at Frankfurt a/M, November 11, 1927, when he said that his organization "will be able to produce easily the raw materials for synthesis of rubber and gutta-percha by contact (or catalytic) synthesis," and that application had been made for patents. Weinberg referred to raw materials for synthesis of rubber and not to the finished product.

Fritz Hoffmann, of Breslau, is at present identified with advanced research on synthetic rubber, and is believed to be engaged in producing synthetic isoprene from *p*-cresol and passing it through  $\beta$ -methyladipic acid. During the war synthetic rubber was produced in Germany at the rate of probably 2500 tons annually, one-eighth of Germany's normal consumption. A special plant was erected for the purpose at Leverkusen, using calcium

carbide, but the process had to be abandoned after the war as non-commercial. The synthetic rubber, moreover, decomposed in the air, and was not susceptible to vulcanization. However, Professor Hoffmann and his colleagues found the organic accelerators and refiners, the "Vulcacite," capable not only of permitting vulcanization, but of rendering the product insensitive to light and air. These auxiliary products have since been of the utmost significance in processing natural rubber, as well as improving the quality of synthetic rubber. Whether research on synthetic rubber has been able to develop its elasticity in comparison with natural rubber seems doubtful.

Undoubtedly the German Dye Trust has succeeded in cheapening the costs of the basic hydrocarbons, but natural rubber producers could lower prices without loss, and be strong competitors of a synthetic venture.



# LACQUERS AND SOLVENTS

Papers presented before the Division of Paint and Varnish Chemistry at the 74th Meeting of the American Chemical Society, Detroit, Mich., September 5 to 10, 1927

## Solvent Structure and Solvent Action

Bruce K. Brown

COMMERCIAL SOLVENTS CORPORATION, TERRE HAUTE, IND.

IN THE manufacture of lacquer it is necessary to produce a homogeneous liquid mixture containing materials that are not completely compatible. While there are a number of solvent liquids that will dissolve either nitrocellulose or varnish gums, frequently solvents that dissolve either solid ingredient separately will not hold both nitrocellulose and gum in the same solution. In practical usage such esters as ethyl acetate, butyl acetate, and amyl acetate are used to dissolve nitrocellulose, but in the completed lacquer there will also be found some diluents—i. e., alcohols and hydrocarbons. In such a liquid mixture it may be presumed that each component plays a definite role.

Attempts have been made to reason that "like dissolves like" and that, since nitrocellulose is a cellulose ester, the best solvents for it will be esters. However alluring this theory may be, it is not well substantiated in practice, since ketones, keto alcohols, hydroxy esters, and ethers are also notably good nitrocellulose solvents. It may also be noted that the gums most used in lacquers are esters, yet to secure complete compatibility of the ingredients of lacquer the presence of hydrocarbons or alcohols is usually required.

There are many instances known in which a mixture of two or more liquids of different molecular structure—that is, having different characteristic solvent groups, such as the carboxyl, carbonyl, and hydroxyl groups—exerts a solvent action on nitrocellulose that is superior to the action of either ingredient separately. It has been reasoned that a single solvent possessing more than one of the solvent groups in its molecule would exert a solvent action superior to that action obtainable with a molecule containing only one solvent group. Keyes<sup>1</sup> has discussed this subject briefly and has cited instances of nitrocellulose solvents which possess more than one solvent group. These he characterizes as two-type solvents.

No doubt there is a broad field of research open to those who can structurally design a solvent to meet a given need. The solvent properties of a liquid for nitrocellulose may be predicted fairly well when the molecular structure of the liquid is known. For example, most esters and ketones are solvents for nitrocellulose and most alcohols and hydrocarbons are not. With some knowledge of this sort it may be possible for chemists to build up solvent molecules containing exactly the proper solvent groups to do a given job. At present, however, there are distressing discrepancies between theory and fact. For example, it has been reasoned that, since nitrocellulose is readily soluble in esters or in ketones, and since most gums are easily dissolved by alcohols, a solvent combining an alcohol group with an ester or ketone group could be employed to dissolve both nitrocellulose and gum; in which case there would be no necessity of using a special gum solvent in formulating a lacquer. But such

reasoning has not yet been supported by experimental evidence.

Diacetone alcohol is a well-known lacquer solvent that contains both a ketone group and an alcohol group. It is, furthermore, an excellent solvent for both nitrocellulose and ester gum if these solutions are made separately. However, when an attempt is made to mix a solution of nitrocellulose and diacetone alcohol with a solution of ester gum in the same solvent, a haze results which persists in the dry film and which can be cured only by adding another high-boiling diluent such as hexalin or "hercosol."

Ethyl lactate is also a nitrocellulose solvent which contains two solvent groups—the ester group and the hydroxyl group. Ethyl lactate dissolves nitrocellulose and also shellac and kauri gum, but ethyl lactate solutions of nitrocellulose and these gums cannot be mixed without producing a cloudy film. The remedy in this case is also to add a high-boiling diluent such as butanol. Exactly the same phenomenon is observed in the case of a one-type solvent such as butyl acetate. Butyl acetate is a good solvent for both nitrocellulose and kauri gum, yet mixtures of these two solutions are not compatible except in the presence of a diluent such as butanol.

The ethyl ether of ethylene glycol provides another instance of a two-type nitrocellulose solvent, since it contains an ether group and a hydroxyl group. This solvent dissolves nitrocellulose and also kauri gum, although it does not dissolve ester gum. However, when separate solutions of nitrocellulose and kauri gum in the ethyl ether of ethylene glycol are mixed, incompatibility is observed and turbid lacquer films are produced. The remedy for this is exactly the same as that used in the case of the one-type solvent, butyl acetate. At the same time, while ester gum is not soluble in ethyl ether of ethylene glycol, it may be readily dissolved in a mixture of that material with some high-boiling diluent.

The instances cited show that however effective a solvent may be in dissolving a variety of single substances, nevertheless, in the practical formulation of lacquers, solvents possessing theoretically desirable solvent groups cannot be relied upon offhand to produce the desired result.

It is not to be denied that two-type solvents sometimes possess unique properties. For example, a nitrocellulose solvent which contains a hydroxyl group will ordinarily dissolve some water, and hence solutions of nitrocellulose, and this material will be more tolerant of water than those made up of simple ester solvents. The practical importance of this particular property is doubtful, however, since water has no proper part in present-day lacquer formulation. It is the hydrocarbons that are most intolerant of water, and a lacquer made up with a two-type solvent and a hydrocarbon is no more tolerant of water than one made up with a one-type solvent and a hydrocarbon.

<sup>1</sup> *Ind. Eng. Chem.*, 17, 1120 (1925).

# Constants of Nitrocellulose Solvents

J. Allington Bridgman

THE WILBUR WHITE CHEMICAL CO., OWEGO, N. Y.

THIS paper describes a study of certain properties of various high-boiling solvents for nitrocellulose which have a bearing on their use in the lacquer industry.

## Evaporation Rate

The rate of evaporation of a solvent or a mixture of solvents affects its value in the preparation of a lacquer, owing to the detrimental effect on the smoothness of the lacquer film when the solvent evaporates too rapidly to allow the film to level out properly after application. Although the boiling range of the liquid gives some indication of the evaporation rate, the vapor tensions of solvent mixtures at room temperature may not be in the same ratio as their boiling ranges. Other factors, such as latent heat of vaporization and formation of constant-boiling mixtures, may also affect the rate of evaporation.

The first work on evaporation rates in this laboratory was carried out with the aid of friction-top cans covers as described by Gardner and Parks,<sup>1</sup> but the results were unreliable, owing chiefly to the tendency of such pans to warp slightly. Even when the pans are not appreciably warped the surface of liquid exposed in the different pans varies as the solvents near complete evaporation.

In order to overcome this difficulty a set of pans of equal weight (35 grams) was made up from aluminum alloy, in which the outside bottom surface was flat but the inside bottom was slightly dished to the center. This dished bottom allowed a fairly even distribution of the liquid in the different pans even though they were resting on a surface that was not exactly level.

The diameter of the pans was 8.3 cm., the depth at the side of the pan was 13 mm., and the amount of dish was sufficient to make the depth at the center 0.7 to 1.1 mm. ( $1/32$  to  $3/64$  inch) greater than at the side. The sides were 1.6 mm. ( $1/16$  inch) thick. It is essential to keep all the pans under as nearly the same conditions as possible and to avoid changes of temperature and drafts in the room or the exposure of any of the pans to direct sunlight. The accompanying graphs (Figure 1) illustrate the type of smooth curve that can be obtained with such pans.

A pan with slightly dished bottom might be used to advantage in all determinations of evaporation rate. The amount of dish might be slightly greater than in the set described.

In view of the importance of the determination of the evaporation rate of solvents and solvent mixtures, it would seem that the American Society for Testing Materials might well consider the adoption of a standard procedure for this determination, to include the type of pan and the size of sample to be employed.

## Viscosity of Lacquer Solutions

A few experiments were carried out to study the effect on the viscosity of lacquer solutions caused by the substitution of a high-boiling ester for an intermediate-boiling ester.

Table I shows the composition of the solutions employed and the viscosity values. The usual steel-ball method was used at a temperature of 25° C. and the times are average values for six or eight readings in each case.

Table I—Viscosity of Lacquer Solutions

EXPT.	BUTYL PROPI- ONATE %	BUTYL ACETATE %	TOLU- ENE %	ETHYL ACETATE %	0.5 SEC. COTTON %	GUM DAMMAR %	Vis- COSITY Seconds	EVAPORATION RATE Min.
1	9.6	..	44.7	22.6	15.4	7.7	1.5	..
2	..	9.6	44.7	22.6	15.4	7.7	1.3	..
3	7.4	..	46.0	25.8	15.8	5.0	1.2	..
4	..	7.4	46.0	25.8	15.8	5.0	1.4	..
5	14.8	..	46.0	18.4	15.8	5.0	1.8	..
6	..	14.8	46.0	18.4	15.8	5.0	1.4	..
7	..	17.0	45.0	17.0	16.0	5.0	1.4	84
8	10.0	..	45.0	24.0	16.0	5.0	1.4	88
9	..	24.0	45.0	10.0	16.0	5.0	1.8	93
10	14.0	..	45.0	20.0	16.0	5.0	1.6	107

The percentage of gum dammar used in the first two experiments was found to be more than could be readily dissolved and was decreased in the remaining experiments. In each pair of experiments the total percentage of ester as well as the percentage of each of the other ingredients was kept the same.

In the first three pairs of solutions butyl propionate was substituted for butyl acetate in equal amounts. A slight increase in the viscosity was noted with the butyl propionate where the percentages were, respectively, 9.6 and 14.8 per cent, while the viscosity was slightly lower with butyl propionate at a percentage of 7.4 per cent. In the last four experiments the total percentage of ester, including the ethyl acetate, was in each case 34 per cent of the weight of the solution. Substitution of butyl propionate for the butyl acetate increased the time required for complete evaporation of the solvent mixture. Experiments 7 and 8 show practically no difference in the viscosity, but in the last pair of solutions the butyl propionate gave a lower viscosity. These experiments show that it is possible to substitute a high-boiling ester for an intermediate-boiling ester and thereby increase the evaporation time without increasing the viscosity.

## Stability of Esters

The stability of the various ingredients of a lacquer is especially important to the lacquer manufacturer when the product is likely to be stored for some time, as is often the case when it is packed in small containers. Decomposition of even one constituent may destroy the usefulness of the lacquer.

A search of the literature showed very little work on the relative stabilities of the various esters, especially the numerous esters at present being used in considerable quantities in the preparation of lacquer.

In this laboratory a number of experiments have been carried out which might have a bearing on the behavior of different esters, but there has yet been no opportunity to compare the results with those which might be obtained when the same esters are used in actual lacquer practice.

**RATE OF SAPONIFICATION**—The rate of saponification of a considerable number of esters was studied by two methods:

**METHOD 1**—A sample of ester weighing from 10 to 12 grams was prepared and diluted with 100 cc. of denatured alcohol formula No. 30. The solution was cooled to 19.5° C. and an amount of 1 *N* aqueous sodium hydroxide solution sufficient to saponify pure ester equal to 40 per cent of the weight of sample was quickly added. The flask was then held in a water bath

<sup>1</sup> *Paint Mfrs. Assocn. U. S., Tech. Circ. 218* (November, 1924).

at 20° C. for 10 minutes, a slight excess of 1 *N* sulfuric acid solution added at once, and the excess of acid then back-titrated to a phenolphthalein end point. By careful manipulation it was possible to obtain close checks by this method. The figures in Table II show the average values from check runs of the sodium hydroxide used up in saponifying the ester.

Table II—Rate of Saponification of Esters (Method 1)

ESTER	NaOH Used Up Per cent
Butyl butyrate (164.5–165.5° C. range)	42.5
Secondary butyl acetate	50.8
"Pentanol propionate"	67.0
Isopropyl acetate	70.7
Butyl propionate (144–146° C. range)	76.3
"Butyl propionate 90"	77.1
"Pentacetate"	77.4
"Butyl propionate No. 85"	84.8
High-test amyl acetate	89.9
Butyl acetate sample 1	93.4
Butyl acetate sample 2	94.3
Butyl acetate (124–126° C. range)	96.1
"Cellosolve acetate"	97.0
Ethyl acetate sample 1	98.5
Ethyl acetate sample 2	98.8

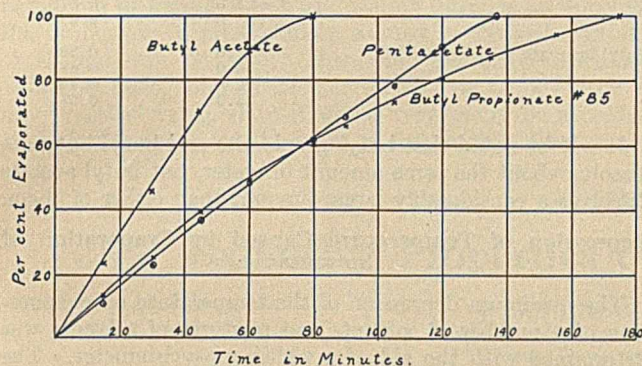


Figure 1—Rate of Evaporation of Esters

**METHOD 2**—In the first experiments, carried out on April 4, 1927, a 25-cc. sample of ester was diluted with 25 cc. of denatured alcohol formula No. 30 and titrated to a phenolphthalein end point with 0.05 *N* alcoholic potassium hydroxide solution at room temperature. A 1-cc. excess of the alkali solution was then added and the time required for the pink color to disappear was noted. In the later experiments, performed on and after July 18, 1927, the quantities were doubled (50 cc. ester, 50 cc. alcohol and 2 cc. excess alkali) and the solutions were adjusted to the temperatures shown in Table III.

Several interesting relations are apparent from a study of the results obtained by the two methods. An increase in temperature gave an increased rate of saponification by the second method, but in general the esters had approximately the same relative rates at the different temperatures. In the first experiments run by the second method the temperature was not recorded, but from the rather slow rate of decolorization of the solutions it must have been much lower than in the later experiments.

It is at once apparent that the order in which the different esters fall is quite different with the two different methods for the study of the rate of saponification. Whereas in the first method, in which sufficient of the alkali was present to saponify 40 per cent of the ester, some of the acetates show a rate of saponification comparable to or in some cases even slower than certain of the propionates, in the experiments in which the amount of alkali is very small all the acetates were more rapidly saponified than the propionates. Furthermore, in the case of both butyl and ethyl acetates, samples from different commercial lots gave widely varying rates of saponification when only the small amount of alkali was present. In the case of the method using the larger amount of alkali, the different samples of the same ester gave very nearly the same rates of saponification. This would at once indicate the presence of a small amount of an impurity much less stable than the acetate ester.

Table III—Rate of Saponification of Esters (Method 2)

Experiments on April 4, 1927

ESTER (25-cc. sample)	INITIAL ACIDITY		TIME TO DECOLORIZE Minutes
	Cc. <sup>a</sup>		
Pentanol propionate	0.5		63
Butyl propionate 90	0.6		44½
Butyl propionate 85	0.3		32½
Ethyl acetate	0.8		25
Cellosolve acetate	0.6		13
Amyl acetate	1.0		8¾
Butyl acetate	0.85		5½

Experiments on July 18, 1927, and later

ESTER (50-cc. sample)	TEMPERATURE 23–24° C.		TEMPERATURE 27–28° C.	
	Initial acidity Cc.	Time Minutes	Initial acidity Cc.	Time Minutes
Pentanol propionate	0.9	21½	1.4	16
Butyl propionate 90	1.2	12¾	1.3	11
Butyl propionate 85	0.9	11½	1.15	8¾
Butyl acetate (124–126° C.)	0.95	9¾	0.9	7½
Butyl acetate sample 1	0.6	9	0.55	7½
Butyl acetate sample 2	2.0	2	2.2	1½
Butyl acetate sample 3	2.7	1½	2.7	1¾
Pentacetate	1.4	4¼	1.5	3
Secondary butyl acetate	2.4	4	2.4	4½
Amyl acetate (high-test)	2.95	2	3.0	1½
Cellosolve acetate <sup>b</sup>	7.6	2¾	7.8	2
Ethyl acetate sample 1	1.1	10¾	1.0	8¾
Ethyl acetate sample 2	1.0	3½	1.1	2¾
Ethyl acetate sample 3	1.0	0¾	1.0	0¾
Butyl acetate sample 1 plus 1% butyl formate	0.65	2¼	0.65	1½
Butyl acetate sample 1 plus 2% butyl formate	0.7	0¾	...	...
Ethyl acetate (0.3% formic acid as ethyl formate)	1.0	6¾	1.1	1½
Ethyl acetate (1.0% formic acid as ethyl formate)	2.6	1½	2.7	0¾

<sup>a</sup> Alkali required to neutralize acidity of sample.<sup>b</sup> End point was difficult to determine.

Since it is well known that lime acetate contains variable amounts of formate and that formate esters are quite unstable, it seems reasonable to suspect that many of the acetate esters now on the market contain varying amounts of formates. Butyl acetate sample 1 is known to have been made from acetic acid which should have contained no formic acid. The rate of saponification of this sample is very near that of the specially prepared sample boiling at 124–126° C., and the addition of only 1 or 2 per cent of butyl formate to this sample greatly increased the rate of saponification by the method using only a small amount of alkali. Samples of ethyl acetate containing known amounts of ethyl formate were obtained through the courtesy of the Sherwin-Williams Company. The ethyl formate, even in the small amounts present in these samples, greatly increased the rate of saponification. Ethyl acetate sample 3, which, of all the

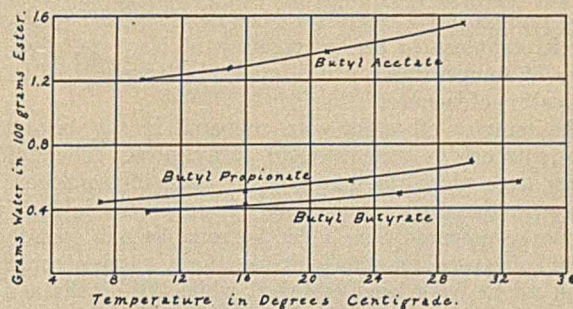


Figure 2—Solubility of Water in Butyl Esters

commercial samples examined, showed the highest rate of saponification, came from a source which would lead one to suspect considerable formate contamination. This method of determining the rate of saponification appears to offer a rapid method for ascertaining whether an acetate ester is likely to be contaminated with formate.

It is also of interest to note that in the case of Cellosolve acetate, the same sample of which was used for both the experiments in April and July, even though on standing a few months the acidity of this sample had increased to a

value several times the original value, the relative rate of saponification was about the same.

The value in lacquer manufacture of the foregoing methods of evaluating the different esters for stability is open to question and the results should be compared with those that might be obtained in practice. It is true that strong alkalies are not present in a lacquer, but basic pigments may be present. While the rate of saponification due to the presence of such pigments would be slow, yet on storage an appreciable amount of crystalline precipitate might be formed or "livering" of the lacquer might result if very readily saponifiable esters, such as formates, were present in small amounts. The relative results with the different esters should be comparable with those obtained when only a very small amount of the ester is saponified by Method 2.

**DEVELOPMENT OF ACIDITY**—Another set of experiments was carried out with several high-boiling solvents to ascertain whether any of them would develop acidity in the presence of a small amount of organic acid. The solutions were made up with 125 cc. of toluene, 50 cc. of ethyl acetate, 75 cc. of the respective high-boiling solvent, and approximately 0.15 cc. of glacial acetic acid. At intervals 25-cc. samples were removed and titrated to a phenolphthalein end point with 0.05 N alcoholic potassium hydroxide solution. The alkali solution was checked against standard sulfuric acid solution at intervals to insure that it did not change in strength during the experiment.

Table IV—Development of Acidity in Presence of Small Amounts of Organic Acid

ESTER	JUNE	JUNE	JULY	AUG.	AUG.	AUG.
	28	29	12	2	19	27
	Cc.	Cc.	Cc.	Cc.	Cc.	Cc.
Butyl propionate 85	5.3	5.3	5.3	5.5	5.5	5.45
Butyl propionate (144–146° C.)	6.4	6.3	6.4	6.6	6.65	6.65
Pentacetate	5.9	5.8	6.0	6.15	5.95	6.0
Pentanol propionate	5.9	6.0	6.1	6.5	6.35	6.4
Butyl acetate	6.6	6.7	6.8	7.0	7.0	7.18
Amyl acetate (high-test)	8.5	8.5	8.55	8.95	9.1	8.9
Cellosolve acetate <sup>a</sup>	7.0 to 7.1	7.6 to 7.7	6.8	7.7	7.8	7.7

<sup>a</sup> End point was difficult to determine.

There was no great change in the acidity of any of the solutions, although a slight change is shown over the period of 2 months.

#### Solubility of Water in Normal Butyl Esters

Determinations were made of the solubility of water in the three normal butyl esters now commonly used as solvents for nitrocellulose in the preparation of lacquers, over the range of temperatures which might be encountered in the application of lacquers.

The samples of esters were prepared in the laboratory from cuts which were already fairly pure. The boiling ranges, over which the samples were taken off from the laboratory fractionating column, are shown in Table V. The samples so prepared were boiled for some time in open flasks before being used, in order to drive out any traces of moisture which might have been adsorbed while the distillate from the fractionating column was being collected.

Preliminary approximate values were obtained by the slow addition of water to an agitated sample of ester held at a nearly constant temperature. The final values were obtained by a method similar to that described by Groschuff.<sup>2</sup> A glass tube of about 100 cc. capacity with a stopcock sealed into one end was prepared. This was weighed and then partly filled with the dry ester and reweighed. The desired amount of water was then introduced and the tube again reweighed. By shaking the tube after it had been warmed up somewhat, the ester was made to dissolve the water

completely, after which the tube was placed in a 2-liter beaker filled with water and equipped with an agitator. By alternate slow cooling and warming, it was possible to determine within about 0.5° C. the temperature at which water was precipitated out of the solution, as shown by the clouding of the liquid which would clear again when the temperature was slightly increased. Table V shows the amount of water dissolved at different temperatures by 100 grams of ester. The curves in Figure 2 were plotted from these values.

Table V—Solubility of Water in Butyl Esters

ESTER	TEMPERATURE	WATER PER 100 GRAMS ESTER
	° C.	
		Grams
Butyl acetate (124–126° C.)	9.5	1.202
	15.0	1.279
	21.0	1.375
	29.5	1.549
Butyl propionate (144–146° C.)	7.0	0.452
	16.0	0.513
	22.5	0.576
	30.0	0.691
Butyl butyrate (164.5–165.5° C.)	10.0	0.380
	16.0	0.424
	25.5	0.497
	33.0	0.574

It will be noted that butyl propionate and butyl butyrate dissolve about the same amount of water, but butyl acetate dissolves a considerably larger amount than either of them.

#### Depression of Temperature Caused by Evaporation of Solvents

The maximum depression of the temperature on evaporation of a number of solvents and mixtures of solvents was determined with the aid of a whirling psychrometer. The experiments indicated that the relative humidity has little effect on the amount of depression of the temperature at a given room temperature. Table VI shows a series of values which were determined at 76.5° to 78° F. (24.7° to 25.6° C.) and an average relative humidity of about 70 per cent.

Table VI—Temperature Depression Due to Solvent Evaporation

SOLVENT OR SOLVENT MIXTURE	TEMPERATURE DEPRESSION	
	° F.	° C.
Amyl acetate (high-test)	7.75	4.35
Amyl acetate (standard)	9	5
Butanol	8.5	4.8
Butyl acetate	10.5	5.8
Butyl propionate 85	7.5	4.2
Butyl propionate 90	6.75	3.75
Cellosolve	5	2.8
Cellosolve acetate	3.5	1.9
Ethyl acetate	28	15.6
Pentanol	6	3.3
Pentacetate	7	3.9
Secondary butyl acetate	14.5	8.0
Toluene	19	10.6
65% Toluene	19	10.6
20% Butyl acetate		
15% Ethyl acetate	18.5	10.3
65% Toluene		
20% Butyl propionate 85	17.25	9.6
15% Ethyl acetate		
65% Toluene	16.25	9.0
35% Butyl acetate		
65% Toluene	16.5	9.2
20% Butyl acetate		
15% Pentacetate	15.5	8.6
65% Toluene		
20% Butyl acetate	15.5	8.6
15% Butyl propionate 85		
65% Toluene		
35% Pentacetate		
65% Toluene		
35% Butyl propionate 85		

While different single solvents showed a considerable variation in the amount of temperature depression in the case of the mixtures of toluene and esters in somewhat the proportions in which they might be used in lacquers the variation was not very marked.

#### Blushing

The data obtained in the last two sets of experiments have a direct relation to the important question of "blushing"

<sup>2</sup> Z. Elektrochem., 17, 348 (1911).

of lacquers. A "blush" is due to the precipitation of one or more of the ingredients of the lacquer during the later stages of drying of the lacquer, and may be a "gum blush" or a "nitrocellulose blush" or both. While the detrimental effect on the appearance of the film is the most noticeable effect of a blush, it is also self-evident that such a film, owing to its lack of homogeneity, will be of inferior strength and durability. Even though a blush is not visible, the strength and homogeneity of the film may be reduced when the blush-resisting ingredients are decreased below a certain point.

The important factor in the prevention of blushing lies in so adjusting the solvents used in the lacquer that the last 10 to 20 per cent of solvent to evaporate from the film shall be, and shall remain as it evaporates, of a composition which will hold both the nitrocellulose and gum in solution. Since in general the high-boiling nitrocellulose solvents used in lacquers are less volatile than toluene, which is now commonly used as a diluent, or the petroleum distillates which are coming into use as diluents, the proportion of nitrocellulose solvent in the last portions of solvent will be high. Therefore, the much discussed "dilution ratio" of high-boiling solvents is of but little if any practical value, since it would very rarely be exceeded in the last few per cent of solvent to evaporate. What would

seem to be of perhaps more importance is that the last solvents to evaporate should have a sufficient solvent action for gums to prevent a "gum blush." It is therefore of advantage to have the high-boiling solvents in the lacquer good solvents for the gums in the lacquer.

The difficulties experienced from blushing when the relative humidity is high appear to be due to the precipitation of the ingredients of the lacquer by water. The depression of the temperature caused by the evaporation of the solvents in the lacquer might cause the precipitation of water on the film. However, the experiments show that the variation in the amount of depression in temperature with various mixtures of toluene and esters in about the proportions used in a lacquer is not very great. It would therefore appear that this is not the factor which explains the marked beneficial effect of the substitution of a high-boiling solvent for a low-boiling solvent on the blush-resisting properties of the lacquer, since the depression of temperature on evaporation is not so greatly affected by such a substitution.

The solubility of water in the solvents however is of considerable importance in the prevention of blushing under such atmospheric conditions, since the data show that butyl acetate will dissolve approximately three times as much water as butyl propionate or butyl butyrate.

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## Explosive Properties of Lacquer-Solvent Vapors

E. G. Richardson and C. R. Sutton

BERRY BROTHERS, INC., DETROIT, MICH.

The range of vapor concentrations in air which are explosive have been determined for a number of typical lacquer solvents. A description of the apparatus used is given. Data are tabulated for solvents used singly and in mixtures of solvents, alcohols, and hydrocarbons similar in composition to the solvent mixes of typical lacquers of spraying consistency. A discussion of the vapor concentration of spray-booth air under various conditions is given, and conclusions drawn regarding the explosive hazards of the concentrations found.

THE phenomenal increase in the use of nitrocellulose products has been accompanied by many inquiries relative to the hazards attendant upon their application by spray methods. It has been the belief of the authors that modern spray booths are sufficiently well designed to provide for removal of solvent vapors rapidly enough to keep the concentration below the explosive range. The chief hazard is believed to lie in the accumulation of mixed nitrocellulose, pigment, and gum dust. Dust accumulations of this kind are known to ignite almost as readily as a gas, owing to the fine state of subdivision.

In this paper experimental data will be presented showing the concentration ranges of explosive mixtures with air of commonly used lacquer solvents, hydrocarbon diluents, and alcohols, and this information will be correlated with the various physical constants of the solvents.

Consideration will be given spray-booth ventilation under conditions found to exist in typical booths with known rates of solvent discharge from spray guns.

### Solvents Used

The solvents were regular commercial-grade materials taken from representative lots.

The distillation ranges given in Table I are taken from the reports of routine tests of the solvents. These figures

represent the first drop and dry point of the range as determined by the standard A. S. T. M. procedure. The flash points were determined by the Tagliabue open-cup method in the laboratory, with the exception of those below 0° C., which were taken from the International Critical Tables, Vol. II. The vapor pressures were all determined by the static method at 25° C. An apparatus was used similar to that described by Moore<sup>1</sup> and by Gardner and Parks.<sup>2</sup>

The volumes of air required for the theoretical combustion of unit volume of solvent in the vapor state and the volume occupied by 1 gram of vaporized solvent at 25° C. and 745 mm. pressure were calculated from the formulas of the pure compounds. These figures are only approximate, but are of value in the interpretation of the data from explosion experiments.

### Description of Apparatus

The apparatus used in determining the explosive limits is shown in the accompanying diagram. *A* is a 100-cc., water-jacketed gas buret as described by White.<sup>3</sup> *B* is a glass reservoir of 250 cc. capacity for storing gas mixtures. *C* is a Pyrex explosion tube, 25 cm. long and 25 mm. in diameter, provided with two sealed-in tungsten electrodes of No. 26 B. & S. gage wire so placed as to form a spark gap of approximately 1 mm. This tube was placed inside a cylinder of wire gauze as a safety precaution. A Ford spark coil and a new 6-volt "Hot Shot" battery furnish a spark across the gap.

All three units are connected with leveling bottles by heavy pressure tubing. Connection between the units is effected by capillary tubing of 1-mm. bore and short pieces of heavy gum-rubber tubing, wired in place. A three-way capillary

<sup>1</sup> *J. Soc. Chem. Ind.*, **39**, 78T (1920).

<sup>2</sup> *Paint Mfrs. Assn. U. S.*, *Tech. Circ.* **237**.

<sup>3</sup> "Technical Gas and Fuel Analysis," p. 15, McGraw-Hill Book Co., 1913.

Table I—Explosive Properties of Lacquer-Solvent Vapors  
(All work carried out at 25° C. and prevailing atmospheric pressure)

No.	SOLVENT	MOL. WT. (PURE)	DISTILLATION RANGE (A. S. T. M.)	FLASH POINT	VAPOR PRESSURE (25° C.)	AIR VOLUME (THEOR.)	VOLUME 1 GRAM AT 25° C. 745 MM.	EXPLOSIVE RANGE			
								Low		High	
			° C.	° C.	Mm.		Cc.	% by vol.	Gram/liter	% by vol.	Gram/liter
1	Ether	74.1	35	-40	526	30	324	1.25	0.0386	10.0	0.308
2	U. S. P. acetone	58	56	-20	225	20	414	2.5	0.0605	9.0	0.218
3	Methanol	32	66	12	116	7.5	749	5.5	0.0734	21.0	0.280
4	Ethyl alcohol	46	76-78	13	60	15	546	4.0	0.0733	14.0	0.256
5	Ethyl acetate	88	72-79	3	104	25	273	2.25	0.0824	11.0	0.403
6	Isopropyl alcohol	60	81-83	12	45	22.5	399	2.5	0.0627	...	...
7	Isopropyl acetate	102	84-97	5	68	35	235	2.0	0.0896	...	...
8	Butyl alcohol	74	113-116	29	9	30	324	a	...	...	...
9	Butyl acetate	116	113-140	22	16	40	207	a	...	...	...
10	Butyl propionate	130	124-161	32	15	47.5	183	a	...	...	...
11	Amyl alcohol	88	117-131	33	8	37.5	272	a	...	...	...
12	Amyl acetate	130	129-148	32	10	47.5	184	a	...	...	...
13	Ethyl lactate	118	127-161	43	4	30	203	a	...	...	...
14	Benzene, 90%	78	77-118	-12	97	37.5	308	1.5	0.0487	9.5	0.308
15	Toluene	92	107-125	8	32	45	261	1.3	0.0498	7.0	0.268
16	V. M. P. naphtha	...	96-154	..	36	...	...	...	0.0499	...	...

<sup>a</sup> Explosive mixture not formed at 25° C.

stopcock,  $S_2$ , facilitates transfer of gas from one unit to another.

$D$  is a small weighing tube in which are placed about 20 grams of solvent for weighing purposes. A similar tube is used as a counterpoise in all weighings.

Because of the solubility of many solvents in water and other liquids, mercury is used as the confining liquid in all parts of the apparatus.

#### Experimental Procedure

Starting with  $B$  filled with mercury, the weighing tube  $D$ , previously weighed filled with solvent, is connected to the apparatus at  $S_3$ .  $L_2$  is lowered and the stopcocks  $S_2$ ,  $S_3$ ,  $S_4$ , and finally  $S_5$  are opened so that a slow stream of air bubbles is aspirated through the liquid in  $D$ . This is continued until  $B$  is filled with vapor-air mixture to the 250-cc. mark. By closing off  $D$  and reweighing it, the quantity of solvent present in  $B$  is determined.

A part of the known mixture in  $B$  is measured into the buret,  $A$ , and diluted with air to any desired extent. It is then transferred to the explosion vessel,  $C$ , where it is sparked and its ability to explode is noted.

Several precautions are necessary in order to secure check

results. All measurements must be started with the capillary connecting tubes filled with mercury. The gas must be followed through the capillary to the vessel to which it is being transferred by the mercury thread. Care must be taken not to subject rich mixtures to excessive pressure while transferring or condensation will result, giving rise to large errors. The bomb and the contained mercury must be frequently dried, also  $L_3$  and the rubber tubing.

It has been found possible with this apparatus to check closely determinations of the limits of inflammability. Close agreement has also been noticed with the work of other investigators in the case of the few solvents for which data are available.

#### Discussion of Data

Wheeler and Whitaker<sup>4</sup> point out differences in the limits of inflammability depending upon the direction of flame propagation. For upward propagation the lower limiting concentration is smaller and the upper limit is higher than for either downward or horizontal propagation.

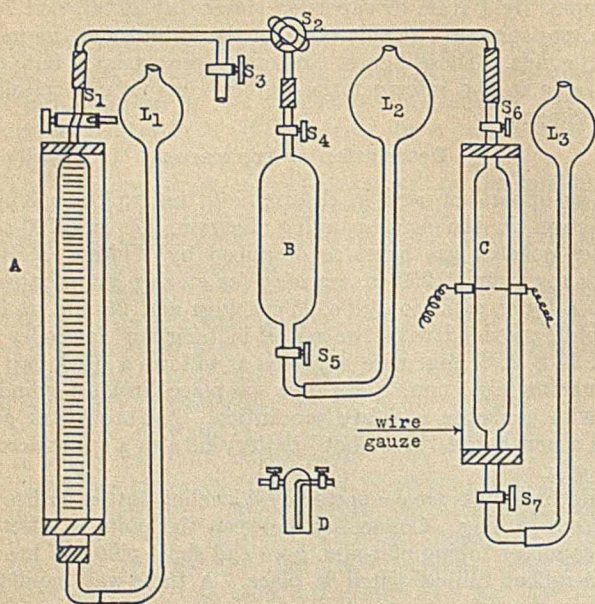
The spark gap of the bomb used in the present work is located in the center of the length of the tube, thus giving an opportunity to observe both upward and downward propagation. The limits, as determined and tabulated, are the extremes—that is, the limiting concentrations which will permit flame propagation in an upward direction.

It will be noticed in Table I that the hydrocarbons tested—benzene, toluene, and V. M. P. naphtha—show small lower-limit values. This is explained by the fact that a large proportion of air is required for their theoretical combustion and by their high calorific value, which makes flame propagation possible in so dilute a mixture. In order that an explosion may occur, sufficient heat must be liberated by the burning gas near the spark to heat the adjacent layers to the ignition temperature. The thermal conductivity of the mixture must be large enough to permit a certain flow of heat to the next layer. Since all the mixtures are very dilute, their thermal conductivity is nearly that of air, and the calorific value is the chief consideration.

Calorific values for a number of solvents are as follows:

	Calories/gram		Calories/gram
Ether	8807	Ethyl acetate	6103
Acetone	7304	Benzene	9960
Methanol	5331	Toluene	10150
Ethyl alcohol	7080		

The values for alcohols and esters are in general much lower than those for the hydrocarbons. Therefore, a greater concentration of these solvents is required to form an ex-



Apparatus for Determining Explosive Properties

A—Gas buret  
B—Gas reservoir  
C—Explosion tube  
D—Liquid weighing tube  
L—Leveling bottles

<sup>4</sup> J. Chem. Soc. (London), 111, 267 (1851).

plosive mixture than for the hydrocarbons. Ether shows abnormal results because of its ability to propagate in a "cold flame." This makes flame spread possible in mixtures of abnormally low vapor concentrations.

Some of the solvents (Table I) do not form explosive mixtures with air at 25° C., as is indicated by their flash points.

Additional experiments were made with these non-explosive solvents. A 3-inch (7.6-cm.) iron pipe was fitted with a spark plug in the side wall. Screw caps with 3/4-inch (2-cm.) holes were placed over the ends. Varying quantities of the solvents were sprayed into the pipe through the small end opening and sparked. No mixture of any of these higher boiling solvents was found which would explode.

It may be observed from the data thus far presented that the low-boiling esters and alcohols and all the hydrocarbons regularly used in lacquer formulation readily form explosive mixtures when present in concentrations of approximately 0.075 gram per liter of mixture for the alcohols and esters and 0.05 gram per liter for the hydrocarbons. It appears that the greater hazard is presented by the hydrocarbons, because of the low limiting concentration for explosive mixture, the high degree of volatility, and the large percentage usually present in lacquer formulas.

#### Behavior of Mixed Solvents

Table II shows a series of mixed solvents, all of which are capable of forming explosive mixtures at 25° C. With the exception of Nos. 1 and 8, they were made up on the basis of 60 per cent hydrocarbon diluent, 30 per cent active nitrocellulose solvent, and 10 per cent alcohol. The active solvents used were limited to three—ethyl acetate, butyl acetate, and butyl propionate—representing the three classes—low, medium, and high boiling. Ethyl and butyl alcohol were taken as typical alcohols. All three hydrocarbons were included in one or more mixes.

Table II—Composition of Mixed Solvents  
(Figures in per cent)

Mixture No.	1	2	3	4	5	6	7	8
Benzene	50	60	20	..	..	20	..	..
Toluene	..	..	40	60	60	40	30	30
V. M. P. naphtha	..	..	..	..	..	..	30	..
Ethyl acetate	50	30	15	15	..	10	..	..
Butyl acetate	..	..	15	..	15	10	..	..
Butyl propionate	..	..	..	15	15	10	30	40
Ethyl alcohol	..	10	5	5	..	..	..	..
Butyl alcohol	..	..	5	5	10	10	10	30
Lower limit for explosive mixture, gram per liter	0.0700	0.0567	0.0714	0.0980	0.0824	0.0620	0.0588	0.0773

The lower explosive limits of these complex solvents in mixtures with air were determined and found to be approximately the same as those for the single solvents of the alcohol and ester types. This was not expected because of the greater volatility of the hydrocarbon diluents and because of the large proportion of them present in the liquid. Mixture No. 8 was included for the purpose of observing the effect of low hydrocarbon content in a mixture with high-boiling solvents. The results obtained here were also surprising, as the explosive limit was found to be lower than for larger hydrocarbon content.

The theoretical lower limit of inflammability of a mixture of two or more gases or vapors can be calculated if the lower limit of each combustible component is known. LeChâtelier has announced a simple formula showing an additive relationship. This formula in its working state is as follows:

$$L = \frac{100}{\frac{p_1}{N_1} + \frac{p_2}{N_2} + \frac{p_3}{N_3} \dots}$$

where  $L$  is the theoretical lower limit of the mixture,  $N_1N_2N_3 \dots$  are the lower limits in percentages of the whole air mixture for each separate combustible gas, and  $p_1p_2p_3 \dots$  are the proportions of each combustible gas so that  $p_1 + p_2 + p_3 + \dots = 100$ .

White<sup>5</sup> has tested this formula by calculating limit mixtures of benzene-toluene-air, acetone-methylethylketone-air, ether-acetone-air, and ether-ethyl alcohol-air. Comparisons were made with experimental results and fairly close agreement was found in all cases.

The formula of LeChâtelier being additive, it follows that solvents, which singly do not give explosive concentrations, may in conjunction with other solvents assist materially in forming explosive mixtures.

Lack of time has prevented further work with mixtures of solvents. Data are needed on the concentrations obtainable when air is saturated with mixtures of various compositions. Other means of obtaining known vapor-air mixes need to be tried. It is hoped that in the near future the Sligh equilibrium-air distillation apparatus,<sup>6</sup> or the modification of it described by Brown,<sup>7</sup> may be tried. It is thought that this apparatus will be very satisfactory for the production of known vapor concentrations of mixed solvents.

#### Spray-Booth Ventilation and Solvent Concentration

A check was made of the air being drawn through each of two standard-type spray booths, 5 by 7 by 6 feet, manufactured by a well-known maker of spray equipment. Anemometer tests showed a flow of 7100 cubic feet of air per minute in booth 1 and 8100 cubic feet per minute in booth 2.

These booths are equipped with 24-inch air ducts and close-fitting ten-blade fans running at approximately 1500 r. p. m.

A familiar type of siphon-feed spray gun was found to deliver 168 grams per minute of mixed solvent when opened wide. Solvent mixes 4 and 5 were used. Assuming uniform distribution of this amount throughout the 7100 cubic feet of air passing through booth 1, the resulting concentration is approximately 0.00084 gram per liter, or about one one-hundredth of the concentration necessary for explosion.

Experiments were made with pressure-feed guns. A wide range of ejection rates are possible with this type, depending upon gun adjustment and liquid pressure. The maximum practical ejection rate was found to be not more than five times that for the siphon-feed gun. If this quantity is assumed to be completely vaporized and evenly distributed throughout the volume of air passing through the booth in the same length of time, the resultant vapor concentration is still much below the lower limit.

Samples of spray-booth air were drawn from the duct back of the fan, where mixing is most complete, while mixed solvent was being sprayed under typical operating conditions. The samples drawn were tested in the bomb and were found incapable of exploding.

It is evident that explosive concentrations are possible in certain areas inside the booth in spite of the most efficient ventilation—as, for example, directly in front of the spray gun. However, flame propagation is not liable to occur in this region owing to the excessive cooling of the expanding air and to the rapidity of the current. These factors have been demonstrated to be sufficient to keep gases cooled below their ignition temperature even in the vicinity of a spark.

<sup>5</sup> *J. Chem. Soc. (London)*, **121**, 2561 (1922).

<sup>6</sup> *J. Soc. Automotive Eng.*, **19**, 151 (1926).

<sup>7</sup> *University of Michigan, Eng. Res. Bull.* **7** (May, 1927).

### Conclusions

1—The apparatus devised is, in the main, satisfactory for the determination of explosive limits of single solvents and of mixtures of solvents at ordinary temperatures.

2—Solvents of the alcohol and ester types require a greater concentration than do the hydrocarbon diluents.

3—The medium- and high-boiling alcohols and esters (distillation ranges starting at 115° C. or above) are not capable of forming explosive mixtures at ordinary temperatures.

4—Mixtures of solvents containing moderate proportions of hydrocarbons readily form explosive mixtures with air, even though the alcohol and ester are of the higher boiling types.

5—Ventilation was found to be adequate in the booths tested to keep vapor concentrations much below explosive limits.

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- 16—Kratz and Rosecrans, "Study of Explosions of Gaseous Mixtures," *University of Illinois, Eng. Expt. Sta., Bull.* **133** (1922).
- 17—Wheeler, "Ignition of Gases," *J. Chem. Soc. (London)*, **125**, 1858 (1924).
- 18—Mason and Wheeler, "Ignition of Gases," *Ibid.*, p. 1869.
- 19—Wheeler, "Ignition by Induction Sparks," *J. Chem. Soc. (London)*, **127**, 15 (1925).
- 20—White, "Limits for the Propagation of Flame in Inflammable Gas-Air Mixtures," *Ibid.*, p. 48.
- 21—Brown, "Relation of Motor Fuel Characteristics to Engine Performance," *University of Michigan, Eng. Res. Bull.* **7** (1927).

## Some Observations on the Consistency of Lacquers

Chas. D. Bogin and Carson W. Simms

COMMERCIAL SOLVENTS CORPORATION, TERRE HAUTE, IND.

THE general importance of the consistency or, to use an older term, viscosity of lacquers in their application is undoubtedly known to everyone in the industry, but there is reason to believe that the great influence of this property is not appreciated and that its consideration does not enter into the routine of formulation and production to the extent that it deserves. Therefore, in the present paper the following factors relating to the consistency of lacquer solutions have been discussed:

- (1) The importance of the consistency of both brush and spray type lacquers in their application.
- (2) Relation of the concentration of nitrocellulose to the consistency of the solution and the bearing of this property on lacquer formulation, especially on the selection of solvents.
- (3) Effect of pigments on lacquer consistency.
- (4) Variation in viscosity of commercial nitrocellulose.
- (5) Effect of aging on the consistency of lacquers and its importance in the marketing of brushing lacquers.

### Effect of Consistency on Application of Lacquers

The setting of a brush lacquer film is due primarily to the rise in consistency which follows the evaporation of the solvents, and it is therefore not surprising to find that the brushing time of a lacquer is dependent to a considerable extent upon its initial consistency. Experiments, the results of which are given in Table I, confirm this. The consistency figures are empirical, being reported in percentages of the viscosity of the standard—c. p. glycerol at 25° C.

CONSISTENCY DETERMINATIONS—These determinations have been made by the outflow pipet method for the determination of viscosity, using pure glycerol as a standard of reference. Within the limits of these experiments such factors as the kinetic-energy correction, etc., are negligible and fall well within the experimental error.

BRUSHING TIME—As reported in the text this is an empirical

figure and is determined in the following manner: Ten cubic centimeters of the material to be tested are flowed onto a rectangular glass plate 8 by 14 inches (20 by 36 cm.) and brushed and cross-brushed with a 1-inch (2.5-cm.) brush which had been wetted in the lacquer and dried by pressing between sheets of paper. A number of trials are made, varying the time of brushing, and the maximum number of seconds which the lacquer can be brushed out without leaving brush marks is taken as the brushing time. Standard brushed plates are often used for comparison. In performing this test care is taken not to overlook the phenomenon commonly called secondary flow, as otherwise a false end point may be obtained.

CALIBRATION STANDARD—The requirements of a viscometric calibration standard are constancy of quality and viscosity. Glycerol fulfils the first requirement excellently, since it is easily purified by distillation and chemical treatment. Its viscosity, however, is greatly affected by the presence of water and for this reason it was rejected as a standard by Herschel<sup>1</sup> and Kolver.<sup>2</sup> The use of 85 per cent glycerol was suggested by Herschel, since this mixture neither absorbed water nor lost it by evaporation. The present writers believe a mixture of this composition would be very suitable. Bawtree<sup>3</sup> states that the internal stresses within the glycerol molecule make that compound unsuitable as a standard.

Castor oil has been frequently proposed as a standard, and according to Deering and Redwood<sup>4</sup> various samples differ but little in viscosity. This finding, however, was made on Indian oils, the methods of production of which are old and standardized. With the ever changing methods of growth and extraction which may be expected in the United States, too much confidence should not be placed in the properties of a product which is not subject to purification by chemical methods. The viscosity of castor oil, furthermore, varies greatly with the temperature—about 9 per cent per degree Centigrade. Castor oil is also recommended by Higgins and Pitman<sup>5</sup> as being the most

<sup>1</sup> *Bur. Standards, Tech. Paper* **112**.

<sup>2</sup> *Z. deut. Öl-Fett-Ind.*, **40**, 677 (1920).

<sup>3</sup> *J. Oil Colour Chem. Assoc.*, **3**, 109 (1920).

<sup>4</sup> *J. Soc. Chem. Ind.*, **13**, 959 (1894).

<sup>5</sup> *Ind. Eng. Chem.*, **12**, 587 (1920).



suitable. According to Fulweiler and Jordan,<sup>6</sup> castor oil showed an increase in viscosity of 0.33 per cent upon standing 24 hours.

Ethyl alcohol-water mixtures, proposed by Bingham and Jackson,<sup>7</sup> are not adaptable for our use owing to their extremely low viscosity.

Table I—Relation between Consistency and Brushing Time

LACQUER	CON-SISTENCY	BRUSHING TIME
	Per cent	Seconds
(1) 1/2-second nitrocellulose in butyl acetate	124	70
	62	105
	31	130
(2) 1/2-second nitrocellulose in butyl acetate + toluene	75	60
	36	85
	16	118

The results indicate that a fourfold increase in the consistency of a given lacquer reduces its brushing time almost one-half. The range of consistency values used in these experiments includes most commercial brushing lacquers which the writers have examined, their average consistency being about 50 per cent. Two lacquers of equal consistency may have, of course, widely different brushing times owing to variation in other factors such as solvent composition.

That the influence of the consistency on the brushing time does not seem to be given consideration in some instances in lacquer formulation is indicated by the results (Table II) obtained in the examination of three samples of commercial brushing lacquers produced by the same manufacturer.

Table II—Variation in Lacquers Produced by Same Manufacturer

LACQUER	CONSISTENCY	BRUSHING TIME
	Per cent	Seconds
(1) Black	25	140
(2) Clear	62	105
(3) Blue	116	75

This variation in consistency is greater than the range used in the writers' experiments. It may possibly be traced to a number of causes. Different batches of nitrocellulose may have been used and no allowance made for the often considerable normal differences in their viscosities. In the case of lacquer (1) it is probable that the thickening effect of the black pigment was not taken into account. Perhaps slight variation in the concentration of the nitrocellulose may be partly responsible for the differences. Whatever the reason, the result is a variation wide enough, in the writers' opinion, to give at one end a lacquer too fluid for brush application and at the other a product too thick to allow adequate brushing time. It therefore would seem advisable to standardize brushing-lacquer formulas on the basis of consistency and adjust each batch of lacquer to the standard consistency by dilution with thinner. It will be shown later that ordinarily this practice will not involve any large variations in the proportion of solids in the lacquer.

For spray application, also, the consistency of a lacquer is found to be an important item, as shown by results of tests on the effects of consistency on sprayability given in Tables III and IV.

Comparing lacquers (1), (2), and (3) in Table III, it is evident that an increase in viscosity necessitates a correspond ing increase in spraying pressure. A satisfactory spray is obtained at 20 pounds (1.4 kg. per sq. cm.) air pressure with lacquer (3), while 50 pounds (3.5 kg. per sq. cm.) are required with lacquer (2), which has a consistency 2.5 times as great as that of lacquer (3). From Table IV it may be said that, for a given air pressure, an increase in consistency reduces the volume of lacquer sprayed. These changes in

the character of the atomization also influence flow, orange peel, blushing, and the general behavior of the lacquer in the process of application.

The ultimate adjustment of consistency in spraying lacquers is usually not performed by the lacquer manufacturer, as with brush lacquers, but by the lacquer user in his thinning operation. Here, however, the recommendations of the lacquer maker are usually followed. Spray-lacquer thinning in most establishments is controlled by the use of hydrometers. There are a number of objections to this method. First, a very delicate instrument and an accurate determination are necessary, since the specific gravity of lacquer is about 1.0 to 1.1 and that of the thinner 0.85. Second, but still more important, specific gravity is not a true measure of the consistency of the lacquer.

Table III—Spraying Behavior of Solutions of 1/2-Second Nitrocellulose in a Mixture of 25 Per Cent Each of Butyl Acetate, Ethyl Acetate, Toluene, and Benzene

SPRAYING PRESSURE	LACQUER 1	LACQUER 2	LACQUER 3
	Nitrocellulose Consistency		
	18% NC <sup>a</sup> = 155%	15% NC <sup>a</sup> = 66%	12% NC <sup>a</sup> = 28%
Lbs./sq. in.	Kg./sq. cm.		
10	0.7	No spray	Dry spray
20	1.4	No spray	About same as 60 lbs. (4.2 kg.) on lacquer (1)
30	2.1	No spray	Almost O. K., slow spray necessary
40	2.8	Dry spray	Better
50	3.5	Very slow spray	Good liquid spray
60	4.2	Gelled film, no flow	Heavy spray
			Very heavy spray

<sup>a</sup> For the sake of brevity per cent has been used in connection with the non-volatile concentration to mean grams per 100 cc. of solvents or solvent mixture. This applies in all cases where per cent nitrocellulose (NC) or per cent pigment, etc., is mentioned.

Table IV—Volume of Lacquer Expelled by Gun per Minute with Solutions of Nitrocellulose in Butyl Acetate

SPRAYING PRESSURE	CONSISTENCY				
	28%	41%	55%	87%	
Lbs./sq. in.	Kg./sq. cm.	Cc.	Cc.	Cc.	Cc.
10	0.7	37	32	25	20
20	1.4	95	82	60	55
30	2.1	137	133	103	93
40	2.8	170	160	145	137

In the writers' opinion a direct measurement of the consistency of the lacquer when ready for spraying would give a much more efficient control of the thinning operation. The only apparent obstacle to the adoption of the viscosity method of dilution control seems to be the lack of a cheap, foolproof, easily read viscometer. The following are suggested as part of the requirements of such an apparatus: It should have an orifice made of non-rusting metal; be provided with an overflow petcock on the side to make the measurement of the volume automatic; and, by the use of interchangeable orifices, be made to empty in different time periods depending on the accuracy desired. An instrument of the Ford cup type could probably be modified to fit these specifications. Since it may be difficult to duplicate orifices with sufficient accuracy, the instrument should be standardized against a known, pure liquid. Chemically pure glycerol has been used for this purpose and is apparently suitable. It is easily obtained in pure form and does not change in viscosity on storage. In using this method the instrument maker will standardize the instrument against glycerol at 25° C., and the number of seconds thus found may be designated as its glycerol number. The lacquer manufacturer or the works superintendent, in his thinning directions, will instruct the operators to thin the lacquer until its consistency equals a certain percentage of that of glycerol at 25° C., say 55 per

<sup>6</sup> Ind. Eng. Chem., 14, 723 (1922).

<sup>7</sup> Bur. Standards, Sci. Paper 298.

cent. The temperature at the time of the consistency determination can be neglected if the thinning is done at the time and place of spraying, since the consistency under the conditions of spraying is the required value.

#### Relation between Concentration of Nitrocellulose and Resultant Consistency

Data on the relation between the concentration of nitrocellulose and the consistency of lacquers are given in Table V.

PROCEDURE—Nitrocellulose sufficient to produce a solution of the maximum viscosity for testing is weighed into a bottle and dissolved in the solvent mixture with the aid of shaking. The bottle must be large enough to allow dilution to at least three times the volume of the solvents originally added. It is the writers' practice to let the solution stand at least 24 hours before making the initial consistency measurement. After the initial consistency is determined, the solution is diluted with a small amount of the solvent mixtures and shaken, and another measurement is made. This process of dilution, shaking, and testing is continued throughout the whole desirable range. By using this method of dilution one is able to eliminate such errors as might be introduced by weighing or by different samples of nitrocellulose.

Table V—Consistency vs. Concentration<sup>a</sup>

CONCENTRATION OF NITROCELLULOSE	CONSISTENCY OF SOLUTION COMPOSED OF:			
	BuAc 50 Toluene 50	BuAc 50 BuOH 50	BuAc 35 Toluene 65	BuAc 25 BuOH 10 EtAc 12.5 EtOH 7.5 Toluene 45
Grams/100 cc.	Seconds	Seconds	Seconds	Seconds
<b>1/2-second</b>				
25.0	1551	1110	1098	639
22.2	757	685	638	366
20.0	508	433	427	238
18.2	309	273	311	162
16.7	189	196	214	118
15.4	131	150	158	86
14.3	95	111	113	63
13.3	73	90	92	47
12.5	57	68	69	41
11.8	51	58	55	34
10.8	41	44	43	28
10.0	29	36	33	21
8.9	21	27	25	15
8.0	15	20	16	11
6.7	9	13	11	8
<b>12-second</b>				
10.0	1119			
9.1	721			
8.3	489			
7.7	357			
7.1	257			
6.6	180			
5.7	113			
5.0	62			
4.0	34			
3.0	15			
<b>30-second</b>				
8.0	1402			
7.3	780			
6.7	542			
6.2	384			
5.7	287			
5.3	220			
4.4	98			
4.0	70			
3.2	38			

<sup>a</sup> Values in horizontal columns are not strictly comparable, owing to use of different samples of nitrocellulose for each group of determinations.

Table V shows the very pronounced rise in consistency with an increase in cotton concentration. In the interval 7 to 10 per cent, which is about the concentration of a spray lacquer after dilution, an increase of 2 per cent of 1/2-second nitrocellulose approximately doubles the consistency. For nitrocellulose of higher viscosity these relations hold qualitatively but not quantitatively, as is to be expected, since the whole range of consistency from zero to infinity is covered in this case by concentration of nitrocellulose from 0 to (estimated) 15 per cent, while for 1/2-second nitrocellulose this consistency range corresponds to concentrations from 0 to 50 per cent nitrocellulose.

The foregoing facts have an important bearing on a number of problems of lacquer formulation. As mentioned pre-

viously, the adjustment of the consistency of brushing and spraying lacquers does not materially affect the proportion of solids. Evidence for this statement is in Table V, which shows that a variation of only 1 per cent in the proportion of solids changes the consistency by 50 per cent, an amount sufficient to alter materially the working qualities of the lacquer.

A still more interesting conclusion from Table V is the relatively small effect of the nature of the solvent on the consistency of the lacquers as compared with the effect of small variations in the concentration of the nitrocellulose. Also, commercial lacquers are generally quite similar as far as solvents are concerned, the majority being built up on the same skeleton formula which represents 60 or 70 per cent of the solvents. For this reason the effect of consistency variations caused by solvent changes is further limited. As an illustration, the skeleton formula consisting of a mixture of 20 per cent butyl acetate and 45 per cent toluene was combined with 35 per cent of various solvents. The effect on consistency is shown in Table VI. It will be seen that the maximum consistency is only 62 per cent higher than the minimum, a variation which in the case of these solutions can be fully compensated by changing the nitrocellulose concentration from 10 to 9 per cent. The writers believe, therefore, that in the formulation of lacquers the effect of solvents on consistency can be to a great extent eliminated from consideration. An understanding of this fact should be of considerable advantage since it permits greater freedom in the choice of solvents.

Table VI—Effect of Solvents on Consistency

LACQUER	10 GRAMS 1/2-SECOND COTTON PER 100 CC. OF SOLVENTS COMPOSED OF:					CONSISTENCY (AV. 4 DETNS.)
	BuAc	BuOH	EtAc	EtOH	Toluene	
	Per cent	Per cent	Per cent	Per cent	Per cent	Seconds
1	25	10	12.5	7.5	45.0	95
2	25	10	12.5	...	52.5	102
3	25	10	..	7.5	57.5	115
4	25	10	..	...	65.0	156
5	25	..	7.5	...	67.5	141
6	20	..	12.5	7.5	60.0	112

In order to show that the relation between concentration of nitrocellulose and consistency is independent of the nature of the solvent, the consistencies of the 25 per cent solutions of 1/2-second cotton given in Table V have been used as 100 and the lower concentrations expressed in percentage of these figures (Table VII).

Columns 3 to 5 give fairly good agreement, showing that the effect of changing the concentration of 1/2-second cotton in the three solvent combinations is proportionate.

The figures in column 2, on the other hand, are higher for large concentrations of cotton and lower for small concentrations. The discrepancy is probably due to lack of uniformity in working conditions.

The data in columns 3 to 5 were plotted against concentrations of 1/2-second cotton in Figure 1 and a smooth curve was drawn through the points. An expression for this curve was derived by:

- (1) Method of selected points
- (2) Method of averages
- (3) Method of least squares

The following equation was obtained:

$$V_{rel} = \left( \frac{C + 10.1}{17.3} \right)^{6.5}$$

in which

- $C$  = concentration of 1/2-second nitrocellulose in grams per 100 cc. of solvent  
 $V_{rel}$  = relative consistency of the solutions

It is clear that if the consistency in seconds of any of the solutions discussed is known for one concentration of  $1/2$ -second cotton, the approximate consistency for another concentration can be obtained from the curve or equation.

In order to gain an idea of how closely the equation fits the experimental data in column 3 to 5 of Table VII, calculations were made of the relative consistencies corresponding to the concentrations of the cotton used. The results are given in the last column.

The equation is offered as giving a very fair picture of the data obtained, but it should be understood that it is purely empirical and that no theoretical significance is attached to it.

The figures in Table V for 12- and 30-second cotton can, in the manner used for  $1/2$ -second cotton, also be transformed to give relative data. The results are given in Table VII. It was found that when the range of cotton concentrations representing relative consistencies up to 100 was properly chosen, and the points were plotted in Figure 1, the curves through them were identical with the curve for  $1/2$ -second cotton.

Table VII—Relative Consistency of Various Solutions of Nitrocellulose

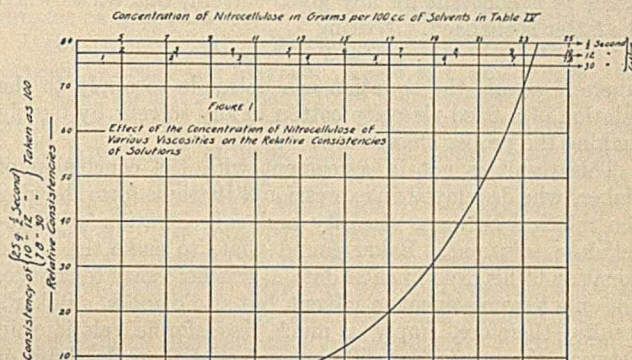
CONCENTRATION OF COTTON	RELATIVE CONSISTENCIES				
	BuAc 50 Toluene 50	BuAc 50 BuOH 50	BuAc 35 Toluene 65	BuAc 25 BuOH 10 EtAc 12.5 EtOH 7.5 Toluene 45	Calcd. from equation
Grams/100 cc.	Per cent	Per cent	Per cent	Per cent	Per cent
$1/2$ -second					
25.0	100	100	100	100	98.2
22.2	49.0	62.0	58.2	57.3	57.5
20.0	32.8	38.2	38.8	37.5	36.3
18.2	20.0	24.6	28.3	25.3	25.1
16.7	12.2	17.6	19.5	18.5	17.0
15.4	8.4	13.5	14.4	13.5	12.3
14.3	6.1	10.0	10.3	9.9	9.3
13.3	4.7	8.1	8.4	7.4	7.0
12.5	3.7	6.1	6.3	6.4	5.5
11.8	3.3	5.2	5.0	5.3	4.7
10.8	2.7	3.9	3.9	4.4	3.5
10.0	1.9	3.2	3.0	3.3	2.6
8.9	1.4	2.4	2.3	2.4	1.9
8.0	1.0	1.8	1.5	1.7	1.4
6.7	0.6	1.2	1.0	1.3	0.9
12-second					
10.0	102.0				
9.1	64.9				
8.3	44.6				
7.7	32.5				
7.1	23.4				
6.6	16.4				
5.7	10.3				
5.0	5.7				
4.0	3.1				
3.0	1.5				
30-second					
8.0	111				
7.8 <sup>a</sup>	100 <sup>a</sup>				
7.3	80.0				
6.7	55.6				
6.2	39.4				
5.7	29.4				
5.3	22.6				
4.4	10.1				
4.0	7.2				
3.2	3.9				

<sup>a</sup> Interpolated.

It was mentioned above that a given consistency range of a solution corresponds to different ranges of nitrocellulose concentration, depending on the viscosity of the dissolved cotton. This being the case for consistencies in seconds, it must also be true for the relative consistencies. The point is illustrated in Figure 1, where a different abscissa scale is used for each of the cottons of different viscosity. It is seen that the relative-consistency interval up to 100 corresponds to a range of 25 grams (per 100 cc. of solvents) of  $1/2$ -second cotton, 10 grams of 12-second cotton, and 7.8 grams of 30-second cotton.

By following the change in consistency of a solution of nitrocellulose as the solvents evaporate, one obtains a picture of the behavior of a lacquer during drying. The data in

Table V can be stated in a form that will make it possible to follow the drying process. Let us consider a solution of  $1/2$ -second cotton in 35 butyl acetate-65 toluene, and assume a spraying lacquer containing 6.7 grams per 100 cc. of solvents is being used (this is a concentration that well may be used in a commercial lacquer). The lacquer will have a consistency of 11 seconds (last line of table for  $1/2$ -second cotton). As the solvents evaporate the concentration of cotton per 100 cc. solvents remaining and the consistency rise, as the data in the table show.

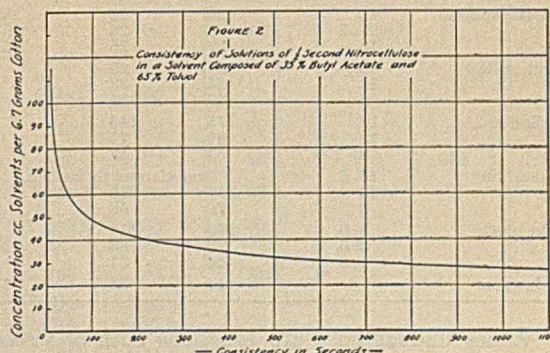


A better picture of the effect of the evaporation is obtained if, instead of stating concentrations in grams of cotton per 100 cc. of solvents, we state the cubic centimeters of solvents per grams of cotton in the original solution—i. e., 6.7 grams. The data then take the form shown in Table VIII.

Table VIII—Consistency vs. Concentration of Solutions of  $1/2$ -Second Nitrocellulose in Butyl Acetate 35-Toluene 65

CONCENTRATION OF SOLVENTS PER 6.7 GRAMS COTTON	CONSISTENCY	CONCENTRATION OF SOLVENTS PER 6.7 GRAMS COTTON	CONSISTENCY
Cc.	Seconds	Cc.	Seconds
100.0	11	46.9	113
83.9	16	43.5	158
70.4	25	40.2	214
67.0	33	36.8	311
62.0	43	33.5	427
56.8	55	30.3	638
53.6	69	26.8	1098
50.5	92		

The data are plotted in Figure 2, which gives a very clear picture of the effect of evaporation of the solvents. Evaporation of the given solution hardly at all, but from this point on the effect becomes very marked, so that by the time the solvents are reduced to 40 per cent of the original amount fur-



ther evaporation causes an immense increase in the consistency. Curves similar to Figure 2 are obtained with other solvents.

The expression derived by the writers relating concentration of dissolved cotton and consistency of the solution has the general form:

$$V_{rel} = h(1 + ac)^k$$

in which, for a given viscosity of cotton,  $h$ ,  $a$ , and  $k$  are constants independent of the solvent,  $c$  is the concentration of the cotton, and  $V_{rel}$  the relative consistency.

Since the relative consistency is proportional to the consistency in seconds ( $V_{sec} = M V_{rel}$ ), we may write:

$$V_{sec} = mh(1 + ac)^k$$

where  $m$  is constant for any given solvent, but varies when the latter is changed. Writing

$$V_{sec} = b(1 + ac)^k$$

where  $b = mh$ , the equation can be made to apply to the solution of a fixed-viscosity cotton in any solvent by merely making the proper change in  $b$ .

This result is not in agreement with the conclusion of Baker,<sup>8</sup> who developed an expression of the same form showing the relation between viscosity and concentration of nitrocellulose solutions. Baker found that, to make the above equation fit his experimental data, it was necessary to change, not only  $b$  from solvent to solvent, but also  $a$  and  $k$ . Baker's results, therefore, imply a much less simple relationship between the curves for different solvents than do those of the present writers. The writers have found, however, that with the proper choice of  $a$  and  $k$  the equation gives very fair agreement with Baker's results when  $b$  alone is changed for different solvents and  $a$  and  $k$  remain constant. The experimental error in work of this nature is such that the agreement obtained by changing the value of  $b$  alone is sufficient for all practical purposes.

#### Effect of Pigments on Consistency

The data in Table IX were obtained with pigments ground in each case in the same clear lacquer. The results show that, while the white pigments and chrome yellow have only slight effects on the consistency of the lacquer, Prussian blue, carbon black, and, to a lesser degree, toluidine red affect the consistency considerably. The difference is probably due to variations in the oil absorption and specific surfaces of the pigments.

Table IX—Effect of Pigments on Consistency

PIGMENT	CONSISTENCY	CONSISTENCY		
		4% Plasticizer	6% Plasticizer	8% Plasticizer
	<i>Per cent</i>	<i>Seconds</i>	<i>Seconds</i>	<i>Seconds</i>
TiO <sub>2</sub> and BaSO <sub>4</sub>	40	37	33	33
	27.5	34	30	30
	15	33	28	26
Zinc oxide	40	33	26	26
	27.5	28	24	23
	15	26	23	23
Lithopone special	40	30	28	28
	27.5	28	26	26
	15	27	25	25
Chrome yellow	18	31	29	
	12	34	33	
	6	37	34	
Toluidine red	18	175	145	
	12	86	75	
	6	53	47	
Prussian blue	16.4	Too viscous to measure		
	12	840	810	
	6	70	68	
Carbon black	4.0	260	410	
	3.0	78	83	
	1.5	56	51	
Clear lacquer		42	38	27

The values undoubtedly are functions both of viscosity and plasticity, the former depending on the cotton in solution and the latter on the finely suspended pigments. The distinction is probably of importance in questions of flow;

the plastic resistance to flow may at times become so great that it is not easily overcome by the very small forces involved in the elimination of brush and spray marks, no matter how long the forces are applied. In the case of viscous resistance, on the other hand, the time is of considerable importance, and if the force is applied for a sufficiently long period the surface will eventually be leveled out fully. In most cases, however, this distinction is not important, since the lacquer film hardens quickly, so that even purely viscous liquids, such as clear lacquer, often fail to flow out fully.

It is interesting to observe the effect of the addition of the blue and black pigments to solutions of 1/2-second nitrocellulose on the concentration-consistency relationship. There are not sufficient data for definite conclusions on this point, but some idea can be obtained from the few figures in Table IX. Thus, doubling the concentration of carbon black (from 1.5 to 3 per cent), as noted in the 4 per cent plasticizer column, increases its contribution to the consistency of the sample from 14 (56-42) to 36 (78-42) or about two and one-half times, while increasing the concentration of Prussian blue from 6 to 12 per cent augments its contribution to the consistency from 34 to 800, or 23-fold. The corresponding consistency increase in going from 12 per cent to 24 per cent nitrocellulose (the proportions which would normally be associated with the above pigment concentrations) is about 15 to 20 times.

The results with the blues and blacks will vary considerably with the grade of pigment. The foregoing figures are therefore only qualitative and are given mainly to show the influence of the nature of the pigments on the consistency of lacquers and the necessity of giving it due consideration in lacquer formulation. The influence of the pigments should be borne in mind, especially by the smaller manufacturers of brush lacquers, who often buy their lacquer prepared and mix it with various pigment combinations.

#### Variations in Viscosity of 1/2-Second Nitrocellulose

The difference in viscosity of various batches of nitrocellulose of a given viscosity is sometimes appreciable, as is shown by the consistencies of 12 per cent solutions of five samples of 1/2-second cotton on hand in the writers' laboratory. (Table X)

Table X—Viscosity of Several Samples of 1/2-Second Nitrocellulose

SAMPLE RECEIVED	CONSISTENCY OF 12% SOLUTION IN 60 TOLUENE-40 BuAc	
	<i>Seconds</i>	
April 10, 1925	225	
October 7, 1926	540	
November 10, 1926	248	
March 7, 1927	426	
April 26, 1927	403	

An examination of Table X will show that a lacquer formula specifying the use of definite proportions of nitrocellulose must produce, at least occasionally, lacquers of a consistency varying from the standard. To eliminate this irregularity the use of small proportions of higher viscosity—30-second or higher—nitrocellulose together with the 1/2-second material is suggested. As the necessary amount of high-viscosity nitrocellulose would at most be very small, the relative amounts of lacquer ingredients—for instance, of the gum and the cotton—would be little affected. Reference tables giving the proportion of higher viscosity nitrocellulose necessary to give a solution of desired consistency could readily be prepared.

Another method of adjusting the consistency of the finished lacquer is to dilute with small proportions of thinner, as suggested in the discussion of brush lacquers.

Incidentally, in sampling nitrocellulose for consistency

<sup>8</sup> *J. Chem. Soc. (London)*, 103, 1653 (1913).

determinations, care must be taken to use the proper proportions of fine and coarse nitrocellulose, as is shown in Table XI.

Table XI—Viscosity of Several Portions of Same Batch of 1/2-Second Nitrocellulose

SAMPLE	FINES		COARSE	
	Seconds		Seconds	
1	187	270	270	270
2	199	270	265	265
3	208	265	265	265
4	218	265	265	265
5	218	267	267	267

#### Effect of Aging on Consistency

The normal aging of lacquer in storage often results in considerable reduction of consistency. Data on this subject are given in Tables XII, XIII, and XIV, where the effect of several months' aging on the consistency of a large number of lacquers is shown.

It will be seen that pyridine, ammonia, and other alkaline bodies greatly accelerate the change, possibly pushing it to a point not attainable in their absence. The effect of sunlight or elevated temperatures is similar. There is some evidence that water and urea have the opposite effect. The change is apparently also catalyzed by other unknown substances sometimes found in lacquer materials, which may account for the occasional extra large reductions in the con-

Table XII—Reduction in Consistency from March 1, 1925, to May 4, 1925 (65 Days)

DESCRIPTION OF LACQUER	NEW LACQUER	OLD LACQUER (9 months old)
	Per cent	Per cent
Blank in dark	24.2	0.0
Blank in sunlight	52.6	40.0
Blank + 0.1% pyridine in dark	49.9	27.1
Blank + 0.1% acetic acid in dark	33.6	4.4
Blank + 0.1% lactic acid in dark	24.2	5.5

sistency of lacquers to which none of the known catalysts have been added. Examples are lacquers 11, 19, 25, and 26 of Series I, Table XIII. There also are variations between different samples of nitrocellulose, as shown in Tables XIII and XIV.

A consistency drop of 20 per cent in 6 weeks of spring weather is about the average. There is evidence that the drop slows up and eventually stops if the above accelerating agents and conditions are absent. This is indicated by values in the last column of Table XII. The point needs further confirmation, however, and is being checked by the experiments in Table XIV, which are to be extended over a long period. The numerous solvent combinations reported in Tables XIII and XIV were used to determine whether the consistency reductions were due to impurities in particular solvents. They evidently were not, since all mixtures observed suffered this reduction in consistency. It apparently occurs with all nitrocellulose solutions.

Most of the data were obtained with lacquers kept in glass

Table XIII—Effect of Aging on Consistency of Various Lacquers<sup>a</sup>

No.	DESCRIPTION OF LACQUER	Cc.	SERIES I—45 DAYS			SERIES II—125 DAYS		
			CONSISTENCY		Reduction	CONSISTENCY		Reduction
			April 30, 1925	June 16, 1925		March 10, 1926	July 16, 1926	
			Seconds	Seconds	Per cent	Seconds	Seconds	Per cent
	24 grams 1/2-second nitrocellulose in:							
1	Butyl acetate	200	100	75	25	273	215	21
2	Ethyl acetate	200	49	37	24	138	112	19
3	Diacetone alcohol	200	253	169	33			
4	Ethyl lactate	200	211	170	20			
5	Butyl acetate	100						
	+ toluene	100	126	96	25	409	316	21
6	Butyl acetate	160						
	+ toluene	140	140	105	25	748	545	27
7	Butyl acetate	100						
	+ benzene	100	134	107	20	433	321	26
8	Butyl acetate	100						
	+ ethyl alcohol	100	113	97	14	295	239	22
9	Butyl acetate	100						
	+ butyl alcohol	100	168	135	20	476	242	49
10	Butyl acetate	150						
	+ ester gum, 50%	48	203	148	27	688	460	33
11	Butyl acetate	150						
	+ dammar, 50%	48	137	83	40	375	283	25
12	Butyl acetate	200						
	+ tricresyl phosphate	12	102	82	20			
13	Butyl acetate	200						
	Butyl phenolate	12	126	101	20	336	246	27
14	Butyl acetate kept in incubator at 97° F. (36° C.)	200	114	76	33	415	186	55
	12 grams 12-second nitrocellulose in:							
15	Butyl acetate	300	125	95	24			
16	Ethyl acetate	300	59	46	22			
17	Diacetone alcohol	300	203	157	23			
18	Ethyl lactate	300	246	209	15			
19	Butyl acetate	150						
	+ toluene	150	200	124	38			
20	Butyl acetate	300						
	+ lactic acid, 0.5%		120	98	18			
21	Butyl acetate	300						
	+ acetic acid, 0.5%		127	83	35			
22	Butyl acetate	300						
	+ nitric acid, 0.5%		108	90	17			
23	Butyl acetate	300						
	+ ammonium hydroxide, 0.17%		116	46	60			
24	Butyl acetate	300						
	saturated with urea		106	78	26	415	375	5
25	Butyl acetate	300						
	+ tricresyl phosphate, 6 grams		155	80	48			
26	Butyl acetate	300						
	+ butyl phenolate, 6 grams		133	85	36			
27	Butyl acetate kept in sunlight	300	125	77	42			
28	100 cc. 4-second stock solution + 50 cc. ethyl acetate + 50 cc. benzene		166	148	11			
29	70 cc. 1/2-second nitrocellulose stock + 80 cc. ethyl acetate + 50 cc. benzene		523	520	26			
30	24 grams A. S. nitrocellulose in 200 cc. ansol		215	157				
31	24 grams 1/2-second nitrocellulose in 200 cc. butyl acetate (80% saturated with H <sub>2</sub> O)		101	95	6			
32	12 grams 12-second nitrocellulose in 300 cc. butyl acetate + 5 cc. NaOH in butyl alcohol		84	52	38			
33	24 grams 1/2-second nitrocellulose in 100 cc. butyl acetate + 100 cc. toluene + 0.05 gram pyridine					427	210	51

<sup>a</sup> All tests made in the dark, except where otherwise specified.

Table XIV—Effect of Aging on Consistency of Various Lacquers

No.	DESCRIPTION OF LACQUER	KEPT IN ROOM			KEPT IN INCUBATOR		
		CONSISTENCY		Reduction	CONSISTENCY		Reduction
		May 16, 1927	August 8, 1927		May 16, 1927	August 8, 1927	
		Seconds	Seconds	Per cent	Seconds	Seconds	Per cent
1	Blank (10% nitrocellulose in solvents)	124 <sup>a</sup>	105	15	124	92	26
2	Blank (10% nitrocellulose in solvents)	124	103	17			
3	Blank 0.1% pyridine	106	67	36			
4	Blank in tin can	131	111	16	134	97	28
5	Blank + 0.2% urea from Mfg. 1	123	110	11	123	92	26
6	Blank + 0.2% urea from Mfg. 2	122	110	11	122	92	26
7	Blank + 0.2% urea from Mfg. 3	122	109	11	122	90	26
8	Blank + 0.2% urea from Mfg. 4	125	117	7	126	99	22
9	Blank + 5% ZnO	150	105	30			
10	Blank + 5% TiO <sub>2</sub> + BaSO <sub>4</sub> pigment	119	107	10			
11	Blank + 2.5% chrome yellow pigment	128	111	12			
12	Blank + 1.2% Prussian blue pigment	121	105	13			
13	Black auto lacquer	118	99	15			
14	10 grams cotton + 40 cc. butyl acetate + 40 cc. toluene + 20 cc. butyl alcohol	217	206	4	217	171	21
15	Adherence standard	120	110	8	120	93	23
16	Commercial brushing lacquer 1				79	68	14
17	Commercial brushing lacquer 2				135	103	20
18	Blank + 20% ester gum	122	80	35			
19	Blank + 20% dammar	130	110	15			
20	Blank + 5% butyl phenolate	116	101	13			
21	12 grams cotton in 100 cc. butyl acetate	159	135	15			
22	12 grams cotton in 100 cc. ethyl acetate	80	69	13			

<sup>a</sup> The original value in each test was taken approximately 1 week after the solutions were made up.

bottles. To check whether the drop in consistency was catalyzed by minute traces of alkali from the glass, parallel tests are being made using tin containers (Table XIV, lacquer 4). The experiments so far have shown a similar drop in the consistencies of the lacquers.

The original determinations of consistency were made after the freshly prepared solutions had been allowed to stand about a week in order to become stable.

This reduction of consistency with time is regarded as of the utmost importance in marketing brushing lacquers. The lacquers are often stored for long periods, and in winter when the demand falls off dealers frequently keep them on top shelves where the temperature approaches blood heat. As a result, the consistency falls very rapidly and may readily be reduced to 50 per cent of the original. If the original consistency of the lacquer was moderate, as recommended at the beginning of this paper, the final consistency would be very low, making application on vertical surfaces difficult.

Research should be conducted to find methods to stop this reduction in consistency. As a temporary measure dealers should be instructed to keep lacquers in as cool a place as possible.

The difficulties discussed apply much less to spraying lacquers because these as a rule are stored for short periods only and often are thinned by viscometric methods.

### Conclusions

1—Consistency materially affects the brushing time of a lacquer. Thus, a fourfold increase in the consistency of a

given lacquer reduces the brushing time to about one-half.

2—An increase in the consistency of a lacquer reduces the volume sprayed at a given pressure and causes a marked increase in the optimum spraying pressure necessary to produce a good film.

3—Recommendations for a standard viscometer are submitted, and the adoption of a consistency method in the control of thinning operations is recommended.

4—A mathematical treatment of the effect of concentration on consistency is given. While the relation obtained is rather complex, it is found that, roughly speaking, an increase of 2 per cent in the cotton concentration doubles the consistency of the solution.

5—Varying the consistency of a lacquer by altering the solvent composition is poor practice, since proper adjustment may be made with less difficulty by changing the nitrocellulose concentration.

6—The viscosities of various samples of 1/2-second nitrocellulose are shown to vary as much as 110 per cent. Different portions of the same batch of nitrocellulose are also shown to vary somewhat in viscosity.

7—White pigments and chrome yellow have only slight effects on the consistency of lacquers, while Prussian blue, carbon black, and to a lesser degree, toluidine red, have a considerable influence.

8—Normal aging of lacquer in storage results in a marked reduction in consistency. Certain impurities frequently found in lacquer greatly accelerate this process.

## Big Reserve of Oil Substitutes

The Secretary of the Interior has announced a survey of possible substitutes for oil, when the natural supply becomes exhausted, which reveals that recoverable oil from oil shales in the United States would amount to approximately 92 billion barrels or nearly ten times the total quantity of the well oil that has been produced in this country to date. He also said the coal and lignite deposits of the country could produce about 104 billion barrels of motor fuel, or in excess of three hundred times the production of motor fuel for 1927.

In making public the second report of the Federal Oil Conservation Board, of which Doctor Work is chairman, dealing with "Possible Substitutes and Shale Oil Development," he expressed the belief that "an oil famine is not imminent, but prudence must always envisage the possibility of an oil shortage."

Other members of the Oil Conservation Board are the Secretary of War, the Secretary of the Navy, and the Secretary of Commerce. A foreword of the second report states that a third

report, "presenting a world-wide survey of petroleum resources," is in the course of preparation. The first report dealt with "general petroleum conditions in the United States."

The possibility of utilizing agricultural products in providing substitute motor fuels, also is discussed. This hinges on two economic problems of supply and price. A detailed analysis of this possibility is presented.

Conclusions reached by technical assistants of the Conservation Board as to the future sources of oil substitutes are contained in the report. With reference to oil-shale deposits, it is stated that they "offer an assured supply of oil for many years if and when the price of petroleum products reaches a level where the extraction of oil from these deposits is profitable."

Regarding oil from coal and lignites, the summary states that "this coal will yield an oil somewhat similar to petroleum and assures us of an adequate reserve of oil for centuries to come, provided, of course, the demand and price would justify its extraction."

## Action of Pigments in Metal Primers

E. J. Probeck and H. W. Battle

JONES-DABNEY Co., LOUISVILLE, KY.

**A**BOUT two years ago the predominating lacquer primers on the market were composed of very small amounts of pigment, a large amount of gum, and varying amounts of nitrocellulose and plasticizer. The theory advocated by most experts was that in order to get adhesion to metal it was necessary to have as much varnish gum present as possible.

### Experimental Tests

**SERIES 1**—To test out this theory the writers made a series of tests, starting with a primer of this nature. The composition is given in Table I.

Black iron panels were thoroughly cleaned and sprayed with a coat of primer. This was allowed to dry 4 hours, and then two coats of lacquer surfacer were applied. The surfacer was stepped down about 1½ inches for the first coat, and an additional inch for the second coat. This gave a weather test on primer, one and two coats of surfacer, and two coats of finishing lacquer.

The lacquer surfacer was made up according to the analysis given in Table I. It was very high in pigment and contained only a very small amount of plasticizer and a comparatively small amount of nitrocellulose, which, of course, made it very easy to sand to a smooth finish. The general trade seems to demand this type of surfacer. It did not have an excessive amount of toughness and was made to sand as near as possible like an oil surfacer.

The lacquer surfacer was thoroughly water-sanded to a smooth surface, and then various types of automobile finishing lacquer were sprayed on. Two full wet coats were used. The lacquer was sanded, rubbed, and polished before exposure in order to get conditions as near as possible to actual methods in vogue in the finishing rooms.

The panels were exposed on the first day of April, 1926, and were taken in on the first of August, 1927, very thoroughly cleaned, and part of the panel polished.

Where oil primers are used, the composition of the base left on the panel after drying usually contains about 2 parts pigment to 1 part varnish base. This shows a very decided difference from the composition of the base of the lacquer where the ratio is about 6 parts vehicle to 1 part pigment.

Table I—Composition of Primers and Surfacers  
(Figures in per cent)

	SERIES 1 PRIMER	LACQUER SURFACER	SERIES 2 PRIMER
Solids	22.50	66.80	22.70
Volatile	77.50	33.20	77.30
ANALYSIS OF SOLIDS			
Pigment	13.35	76.00	39.00
Half-second nitrocellulose	31.10	8.60	30.00
Plasticizer	11.80	3.10	11.10
Gum	43.75 <sup>a</sup>	12.30 <sup>b</sup>	19.90

<sup>a</sup> Half ester and half dammar.

<sup>b</sup> Dammar.

**SERIES 2**—In the second series of tests the amount of pigment was increased at least three times that in the first series; the gum was decreased at least one-half. This gave a primer that was absolutely solid in covering, somewhat flat, and the first indications are that it did not adhere to the metal as well as the other type. Analysis of the primer for the second series is given in Table I.

The same surfacer was used as in the previous series, and the lacquer enamels were similar—that is, they were good durable lacquer enamels for exterior work.

Table II—Composition of Special Panels  
(Figures in per cent)

	PANEL 6	PANEL 7	PANEL 8
Solids	18.70	20.00	18.50
Volatile	81.30	80.00	81.50
ANALYSIS OF SOLIDS			
Pigment	27.10	36.70	32.60
Nitrocellulose	32.20	25.90	29.00
Plasticizer	14.20	12.80	13.00
Gum	26.50	24.60	25.40

**OTHER TESTS**—Three additional panels were run with single coats of different pigment composition—a combination of blues and greens and some of the commonly used white pigments. These broke down very early in the tests, and showed very serious rusting and chalking. All three panels showed excessive chalking and indications of rust in 4 months. In 6 months all showed rust spots and indications of failure. Analyses of these three special panels are given in Table II.

### Conclusion

The results after 16 months' exposure of the panels show conclusively that the primer with a small amount of pigment does not hold up. The primer in Series 1 started to fail in between 3 and 4 months, showing rust spots and then complete disintegration; whereas, in Series 2, even after 18 months, the primer is practically in perfect condition, shows no rust spots, and apparently is an ideal foundation for the lacquer coats. The lacquer enamels in Series 2 are in considerably better condition than those in Series 1. Inasmuch as the same type of lacquer enamels was used, it seems to indicate conclusively that the primer has considerable bearing on the durability of the finishing lacquer enamels. The appearance of the panels indicates that the lacquer enamels in Series 2 were at least twice as durable as those in Series 1. This would give a maximum durability of the entire lacquer system, as indicated in Series 2, of at least three years.

The results also show that the high pigment concentration of the surfacer was too great. Here we have a ratio of about 4¼ parts pigment to one part base. Decreasing the pigment and increasing the nitrocellulose, gum, and plasticizer, would give a tougher film and one that would be harder to sand, but such a film would be more durable and would hold up the finishing lacquer better. As for the lacquer surfacer, a maximum of 55 per cent solids should give the most homogeneous film that would still be workable in automobile finishes.

In the course of this work no attempt was made to make a complete determination of which pigments were the best for lacquer primers. The test indicated that iron oxide of a high state of purity (at least 90 per cent oxide) is one of the best pigments that can be used for this work. Chrome greens and chrome yellows and some of the commonly used white pigments did not give such good results as iron oxide. The results also indicate that a lacquer primer should contain at least 39 per cent pigment to give the proper durability to the entire lacquer system.

# Lacquer Formulation, with Especial Reference to the Use of Cumar

Allen Rogers and Clifford Banta

PRATT INSTITUTE, BROOKLYN, N. Y., AND THE BARRETT COMPANY, PHILADELPHIA, PA.

**T**HIS paper applies particularly to brushing lacquers, although many of our brushing lacquers are also excellent spraying lacquers, the main difference being in the rate of evaporation or drying.

## Components

A lacquer consists essentially of nitrocellulose as the base material, which has been rendered soluble by suitable solvents, and to which have been added diluents, plasticizers, gums, and oils. Sometimes coloring matter is also added. To be commercially applicable a clear brushing lacquer must possess the following qualities:

- (1) It must be clear.
- (2) It must be easily spread with a brush.
- (3) It must have sufficient body to give the desired flow and protection.
- (4) It must not lift or draw on repeated applications.
- (5) When dry the film should be transparent and show no tendency to blush or give a cloudy appearance.
- (6) In most cases it should be capable of rubbing to a fine smooth finish.

That grade of nitrocellulose must be selected which is most suitable for the purpose for which it is to be used. It is now possible to obtain any degree of fluidity by mixing the various grades.

A number of solvents for the nitrocellulose are now available. Of the low-boiling compounds acetone and ethyl acetate should be mentioned. Of the medium boilers butyl-acetate is probably the most largely employed, although butyl propionate and the monoethyl ether of ethylene glycol are finding favor in the trade. The high-boiling compounds, such as ethyl lactate and diethyl oxalate, are used only in limited amounts.

Dibutyl phthalate and tricresyl phosphate are the most commonly employed plasticizers, the chief object of which is to add flexibility to the finished film and to prevent the precipitation of the cotton in the form of a blush or cloud.

Diluents are used to reduce the cost of a lacquer and in proper combination do not destroy its valuable properties. Benzene, toluene, and xylene are the principal diluents, toluene seeming to have the preference. In certain combinations it is possible to use petroleum distillates, but this procedure is not general. The amount of diluent must be very carefully adjusted to the amount and evaporation rate of the solvents.

Another important constituent of modern lacquers is butanol, whose chief purpose seems to be as a blending agent between the diluent and solvent.

Nitrocellulose lacquers in themselves produce a flat finish to the surface of the film. To secure a gloss and give added body it has been found necessary to introduce certain gums and oils. The material most largely used for this purpose is ester gum. This product by itself, however, does not give all of the qualities required, and so other gums and resins, such as dammar, elemi, copal, shellac, and synthetic resins, are usually added. Of these, dammar has been most favorably received in the past. As the natural gums are fairly expensive and have other drawbacks, synthetic materials have come more and more into use.

Among the synthetic resins one which offers exceptional possibilities is cumar. This is a neutral polymerization product made from certain coal-tar naphthas in very large quantities at a minimum cost and of a standard degree of purity. For lacquer manufacture cumar has many decided

advantages. It is cheap. It is hard. It is a clear, light-colored, transparent solid and is not affected by alkalies or acids. It is soluble in all cotton solvents and in practically all diluents except alcohol. Thus far a satisfactory formula with cumar alone has not been developed, but when mixed with ester gum or natural resins it imparts to the film the necessary degree of hardness and produces a gloss and body superior to that obtained from ester gum or ester gum with natural resins. Being acid-proof, alkali-proof, and water-proof to a high degree, it renders the film more weather-resistant than a combination of other gums and resins. Many experiments with cumar combinations indicate that a ratio of 7 parts of ester gum to 4 parts of cumar furnishes a gum content which, on repeated weather tests, gives a superior film. Cumar cannot always be used to replace other gums, but by proper regulation of the formula it may be readily substituted and an improved product obtained.

To give more flow and body to a lacquer there is a growing tendency to replace part of the gum with an oil. This procedure also makes the lacquer work under the brush more like an oil varnish. Linseed oil, either raw, boiled, or blown, is one of the most important oils used for this purpose. Among the other oils should be mentioned castor and rapeseed, which are introduced as either raw, boiled, or blown, China wood oil, pine oil, and Hercosol. The amount of oil added depends largely upon the other constituents, but generally is comparatively small. Too much oil not only retards the drying, but tends to give a soft film and one which is liable to lift on repeated applications.

## Formulation

Let us now see how the component parts of a lacquer are assembled. We will take a typical formula and follow the steps necessary to produce a finished product.

Typical Lacquer Formula		Per cent by weight
	Per cent by weight	Per cent by weight
Nitrocellulose (1/2 sec., wet with 30 per cent of alcohol)	8	Butyl acetate 25
Butanol	10	Dibutyl phthalate 5
Toluene	31	Ester gum 7
Ethyl acetate	10	Cumar 4

The cotton is placed in a suitable container for mixing and the butanol and toluene are added. When well wet the ethyl acetate, butyl acetate, and dibutyl phthalate are added and the mass is stirred until all of the cotton is in solution. The mixture of ester gum and cumar is now introduced and the stirring continued until all of the gums have dissolved. This will give a finished lacquer of the quick drying type, which is clear and ready for use. It may be pigmented by adding the necessary amount of pigment ground in oil, or the plasticizer may be used as a grinding medium, or again the clear lacquer may be placed in a ball mill and the dry pigment thus incorporated.

In the case of a lacquer requiring an oil the formula may be modified by simply replacing 3 parts of the toluene by a suitable oil, or the oil may take the place of a part of the gum mixture. The heavy-bodied oils give more viscosity to the product, but in cases where this is not desired a thin or raw oil may be employed.

This formula is given to show the general type of lacquer in which cumar can be used to advantage. It can be modified, within reason, by the manufacturer to meet his individual requirements.



## Thinners for Nitrocellulose Lacquers

J. G. Davidson and E. W. Reid

CARBIDE AND CARBON CHEMICALS CORPORATION, NEW YORK, N. Y.

New thinners for the ordinary type of nitrocellulose base lacquers are discussed. These thinners differ from the type formerly used in that they contain small percentages of solvents boiling from 135° to 160° C. which replace larger quantities of solvents boiling from 110° to 140° C. These thinners when used with the usual type base lacquer give results comparable in every respect with old type thinners.

THE rise of the automobile-lacquer industry has eliminated many of the problems inherent in the application of the old-time varnish enamels. It has, however, introduced certain new arrangements in the handling of materials that require special methods. For example, nitrocellulose enamels cannot readily be shipped in the form in which they are used, because the pigments and gums tend to settle out in the bottom of the container and it is rather difficult to get them back into solution again with the assurance that no undissolved solid lumps or particles that would mar the finished surface will be present. For this reason automobile enamel is generally shipped as a heavy base lacquer, so thick and viscous that its constituents will not ordinarily separate through the influence of gravity. At the plant this base lacquer is diluted with a thinner, usually in the proportions of approximately 1:1 but sometimes as high as 2:1 or even 3:1.

### Requirements of Lacquer Thinners

For the ordinary type of base lacquer there are certain general requirements that must be fulfilled by any thinner. It must be a solvent for nitrocellulose; otherwise the sudden addition of a large amount of thinner, or drowning as it is familiarly called, will result in precipitation of flocculent nitrocellulose that cannot readily be stirred back into solution. The thinner must not contain any constituents that will be detrimental to the final lacquer, such as solvents that are likely to hydrolyze. It must not present difficulties from the physiological standpoint either by actual toxicity of the vapor or through an unpleasant odor due to impure materials. Lack of odor or pleasant odor are, of course, distinct advantages. It must cut the base lacquer readily and with little stirring and it must produce a mixed lacquer that will work properly in the spray gun. Finally, the solvents must be so proportioned that blushing will not occur under the conditions in which the lacquer is used.

### Prevention of Blushing

In general the usual type of thinner will meet all the requirements except the last, and it is here that most difficulties arise in modern automobile plants. If the thinner does not contain the proper solvents in the proper proportion, moisture is liable to be condensed upon the work under humid conditions or, conversely, some of the moisture present in the original lacquer is not carried off. This brings about the familiar phenomenon of blushing. Inasmuch as the conditions obtaining in humid climates are normally very different than those in dry atmospheres, if the quantity of thinner used is very great, it will pay to formulate a special thinner for each locality. In general, however, this has not proved worth while and most firms content themselves with a summer and winter thinner, the summer thinner having a high blush resistance to cope with the high humidity of summer

and the other having lower blush resistance for use in colder weather when the humidity is low.

The properties of blush-resisting solvents (retarders) are as follows:

- 1—The boiling point is above the boiling point of water.
- 2—They are only partially soluble in water or have the ability to form constant-boiling mixtures with water.
- 3—They are good solvents for nitrocellulose.

Other things, such as solvent power for nitrocellulose, being equal, the amount of blush-resisting solvent that must be used is inversely proportional to the boiling point. Thus, much larger quantities of a solvent boiling at 110° C. must be used than one boiling at 190° C. The temperatures cited are, however, quite extreme and would not generally be advocated. A solvent boiling at 110° C. would evaporate much too quickly unless very large quantities were used, while a solvent boiling at 190° C. would probably evaporate too slowly and leave a soft coating that could not be sanded and polished in the time allowed. Usually forced drying could be used in the latter case, but this is objectionable if the same results can be secured without forcing.

### Composition of Thinners

The general type of thinners hitherto available has had a composition varying approximately as follows: 5 to 25 per cent ethyl acetate, 20 to 40 per cent butyl acetate, 10 to 20 per cent butyl alcohol, and 20 to 60 per cent diluent.

The diluent is usually toluene, but it may be replaced in whole or part by xylene or gasoline. These thinners have been very satisfactory and have only given trouble when attempts have been made to lower the percentage of butyl acetate and butyl alcohol below the limits experience has shown to be necessary.

The development of new nitrocellulose solvents has recently made available a number of new compounds having boiling ranges higher than butyl acetate but still not so high that their evaporation would unduly retard the setting of the lacquer film.

The more prominent of these materials are amyl acetate, which in consequence of its synthetic production has recently become available at prices much lower than formerly, butyl propionate, Cellosolve (ethylene glycol monoethyl ether) and Cellosolve acetate (ethylene glycol monoethyl ether acetate). In the general thinner formula given above the butyl acetate and butyl alcohol can be replaced in whole or in part by smaller quantities of any of these compounds. The relative efficiency of these retarders as blush resistors is approximately as follows: 8 parts of amyl acetate are approximately equal to 6 parts of butyl propionate and 5 parts of Cellosolve acetate. Cellosolve itself presents a special case that will be discussed later.

A general formula that will have a blush resistance of 90 per cent humidity at 90° F. when blended with the usual type of automobile base lacquers is as follows: 10 to 20 per cent ethyl acetate, 5 to 10 per cent Ansol, 10 per cent Cellosolve acetate, and 60 to 80 per cent toluene. The Cellosolve acetate, however, seems to confer a special benefit in the form of better gloss and less orange peel.

Cellosolve itself acts as a retarder up to conditions of approximately 65 per cent humidity at 90° F. As it will no doubt eventually be somewhat cheaper than its deriva-

tive, Cellosolve acetate, it can be used in any amount in the winter time and in the summer where the humidity does not exceed the conditions outlined above. Except when unusually severe humidity prevails half the Cellosolve acetate may be replaced by Cellosolve for summer use. In the winter from three-quarters to all the Cellosolve acetate can be replaced to advantage by the Cellosolve, as it is a very powerful solvent and has a higher dilution ratio than any of the other retarders. It will be understood, of course, that this statement does not hold for brushing lacquers, where percentages of Cellosolve up to 30-40 per cent are used successfully.

How far the subject of new solvents should be investigated is somewhat problematical. Just how much the water solubility of the solvent changes the blush resistance is also an undetermined factor. For example, experiments have shown that the diethyl ether of ethylene glycol which is only partially soluble in water while Cellosolve is entirely so, is a better blush resistor than Cellosolve when used in amounts up to 5 per cent, but quantities in excess of this do not improve the results obtained with this amount. On the other hand, the butylethyl ether of ethylene glycol, boiling at 170° C., which is somewhat more soluble in water than Cellosolve acetate, has approximately the same blush resistance, and may be used in quantities up to 20 or 25 per cent. However, it does not seem to give a surface that has the high gloss produced by Cellosolve acetate.

#### Solvent Power

The solvent power of thinners used in connection with automobile base lacquers must be rather carefully watched. If it is below a certain critical value complete solution of the nitrocellulose is not readily made. Furthermore, on standing over a period as short as 10 to 12 hours the solution may gel or stiffen. The solvent power of the thinner can be calculated by either one of two methods. In the first<sup>1</sup> method the various solvents in common use have been given index values that have been worked out from practical use. The values for some of the more commonly used materials are as follows when toluene is used as a diluent:

Ethyl acetate	1 1/2
Ethyl alcohol (when used in quantities not greater than 10%)	1
Butyl alcohol (when used in quantities not greater than 15%)	1
Butyl acetate	1
Cellosolve	2
Cellosolve acetate	1

When the summation of the percentage of active solvent multiplied by its index value equals 35 or more, the thinner will prove acceptable for use with modern base lacquers.

The second method involves merely a setting forth of the dilution ratios of the various solvents with respect to the diluents used. This system requires the fixing of an arbitrary value for the alcohols, which are not by themselves solvents for nitrocellulose but which increase the solvent power of many of the commonly used solvents. Under this system when toluene is used as the diluent the dilution ratio or the solvent power number of each solvent with respect to toluene is used as the index value. If gasoline is used as the diluent the index values become the dilution ratios with respect to gasoline. The index figures for the materials shown above are set forth below, the diluent being toluene:

Ethyl acetate	3.7	Cellosolve	5.3
Ethyl alcohol	2.0	Cellosolve acetate	2.7
Butyl alcohol	2.0	Butyl propionate	2.8
Butyl acetate	2.6		

With this system the total of the index numbers multiplied by the percentage used should equal 90 in order to

<sup>1</sup> Private communication from H. C. Mougey, General Motors Research Laboratories.

give the same results that the total of 35 gives in the other system. Two examples will illustrate this empirical rule.

#### Example I

COMPOUND	COMPOSITION	INDEX NUMBER		
	Per cent			
Ethyl acetate	15 ×	{ 1.5 = 22.5		
		{ 3.7		
Ethyl alcohol	5 ×	{ 1.0 = 5.0		
		{ 2		
Toluene	70			
Cellosolve	5 ×	{ 2.0 = 10.0		
		{ 5.5		
Cellosolve acetate	5 ×	{ 1.0 = 5.0		
		{ 2.7		
	100	Solvent power...	42.5	106.5

Since the value of this mixture is greater than 35 in one case and 90 in the other, its solvent power will be satisfactory.

#### Example II

COMPOUND	COMPOSITION	INDEX NUMBER		
	Per cent			
Ethyl acetate	5 ×	{ 1.5 = 7.5		
		{ 3.7		
Toluene	70			
Butyl alcohol	10 ×	{ 1.0 = 10		
		{ 2.0		
Butyl acetate	15 ×	{ 1.0 = 15		
		{ 2.7		
	100	Solvent power...	32.5	76.5

As the value of this thinner is less than 35 by Mougey's method and less than 90 by the other, it will not have sufficient solvent power when used with the usual type of automobile base lacquer in the proportion of 1:1.

#### Tests for Suitability in Lacquers

The only test that has given useful information as to the way in which a lacquer thinner will work is a practical test in which large panels are coated under conditions of temperature and humidity that can be controlled. This test is later followed up by actual plant tests in which several automobile bodies are sprayed. It has been found that boiling point curves, specific gravity, viscosity, rate of evaporation, and amount of cooling produced by evaporation are all without inferential value unless applied to formulas that do not involve changes in the active solvent used. When the use of new solvents is proposed, aging tests of panels sprayed with lacquer containing the new solvent are, of course, necessary to determine whether any reaction is set up that will destroy the film sooner than usual. These tests can be quickly secured under an ultra-violet light or from a practical standpoint panels exposed for a period of 6 months will give a very definite indication of what may be expected with reference to the durability of the panel.

So far as Cellosolve and the pure ethers are concerned, there is no question of deterioration. Cellosolve acetate has been investigated very thoroughly with respect to hydrolysis. The results show that under the conditions of general lacquer use it is at least as stable as the esters commonly used. Lacquers containing Cellosolve acetate have stood for many months without developing acidity while panels sprayed with lacquers containing Cellosolve acetate have shown no tendency to break down after having been exposed to the atmosphere over a period which now approximates 9 months.

This question of hydrolysis has been studied very fully and the results of this work will be presented later.

#### Acknowledgment

The authors wish to express their appreciation of assistance extended them during the collection of these data by H. C. Mougey, of the General Motors Research Laboratories, the laboratories of the du Pont Company, and several motor-car manufacturers who cooperated in the full-scale tests made in a production way.

# Determination of Sulfur in Volatile Fuels<sup>1,2</sup>

H. T. Kennedy

BUREAU OF STANDARDS, WASHINGTON, D. C.

SEVERAL methods have been developed for the determination of sulfur in fuels. These include the A. S. T. M. lamp method (D-90-26T), the A. S. T. M. bomb method (D-129-22T) and the Lomax<sup>3</sup> method. The first of these usually gives fair results, is reasonably rapid, and has therefore been adopted as a tentative standard by the American Society for Testing Materials. On certain samples, however, especially those containing carbon disulfide, large deviations are obtained when tests on the same material are made by different operators. The following data,<sup>4</sup> obtained on samples 1, 2, and 3, tested by members of Subcommittee VII of Committee D-2 on Sulfur Determination and Differentiation of this society, illustrate this point:

LABORATORY	SAMPLE 1	SAMPLE 2	SAMPLE 3
1	0.192	0.157	0.201
2	0.190	0.150	0.203
3	0.192	0.152	0.179
4	0.15	0.040	0.300
5			
6	0.194	0.145	0.201
7	0.192	0.120	0.223

As will be observed, the general agreement on sample 1 is excellent. On samples 2 and 3, which are known to contain carbon disulfide, the deviations are too large when it is considered that these figures are the average of two or more determinations from each laboratory. Since the sulfur compounds that occur in motor benzene usually include carbon disulfide, the failure of Method D-90-26T to determine correctly sulfur present as carbon disulfide is a serious defect.

The bomb method, although probably accurate when adequate precautions are taken, has not proved so in practice when applied to motor fuels. It is also time-consuming and not suitable for routine work. However, it is one of the few methods available for products of low volatility.

The Lomax method, similar in principle to Method D-90-26T, appears to correct the tendency of the latter to give low results on carbon disulfide mixtures, but is extremely tedious. Further, as barium sulfate is precipitated from fairly concentrated (5 per cent) solutions of sodium chloride, it is not impossible that the higher results are due in part to adsorption of sodium chloride by the barium sulfate.

In the method described in this paper, the fuel is vaporized in a carbureting device and burned, and the sulfur oxides so produced are absorbed by a sodium carbonate solution of known concentration.

## Apparatus

The accompanying drawing shows the essential parts of this apparatus. The fuel to be examined is contained in and measured by the reservoir *A*, making the weighing of the lamp before and after burning unnecessary. From the reservoir the fuel flows through the special regulator, *B*, which consists of an unbored stopcock, on the cylindrical surface of which is etched a tapering channel. By turning this cock, a channel of varying average width is available to conduct the fuel from the reservoir to the vaporizing chamber and, as it can be utilized through an angle of nearly

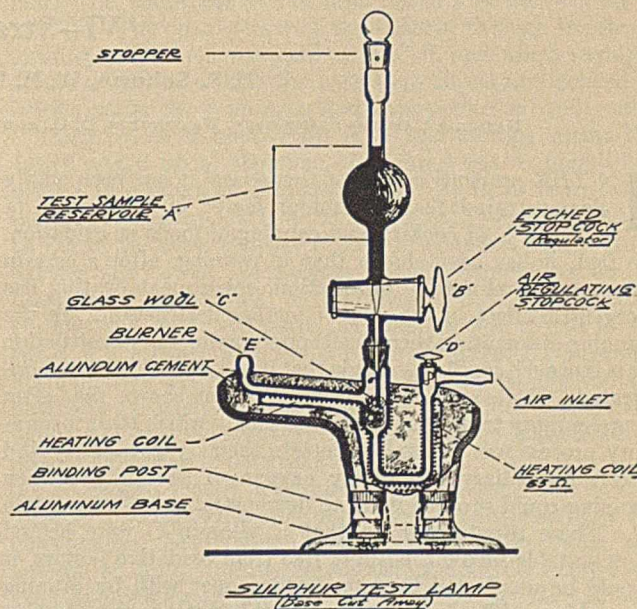
90 degrees, this device affords a delicate and convenient means of adjusting the small flow necessary to maintain a flame.

The fuel then flows on a small plug of glass wool, *C*, from which it is vaporized by a current of hot air passing through the air regulator, *D*, and the mixture is burned at the tip, *E*. The air regulator *D* consists of a cock, the lower edge of which is ground off spirally, and whose position relative to its seat determines the length of a narrow slit which is available for the passage of air. As an angle of nearly 360 degrees can be utilized, this device also affords a convenient means of regulation.

The vaporization chamber is surrounded by a nichrome heating coil of 65 ohms resistance, designed to vaporize the fuel completely and insure that no unvaporized fuel is left on the glass wool. The proper temperature is secured when two sulfur lamps are connected in series across a 110-volt line. The vaporization chamber and heater are mounted in an aluminum casting for convenience in handling.

## Procedure

To determine sulfur by means of this lamp, the heater is switched on a few minutes before the run is to be started, the reservoir is filled conveniently by means of a pipet somewhat above the upper graduation with the fuel to be tested, the fuel and air regulators are adjusted, and the flame is lighted, preferably with an alcohol flame since matches contain a large amount of sulfur. The flame should be approximately  $\frac{1}{2}$



inch (13 mm.) high and colorless or slightly yellow. When the fuel meniscus reaches the upper graduation, the flame is placed under an absorber, as in Method D-90-26T, the suction on which is so adjusted as to accommodate all the products of combustion. No further attention is needed until the meniscus is approaching the lower graduation, when the fuel regulator is so adjusted that the flame is approximately the same height as at the start. This step is necessary to eliminate the effect of a slight lag in vaporization from the glass wool. When the lower mark is reached, the

<sup>1</sup> Received September 27, 1927.

<sup>2</sup> Published by permission of the Director of the National Bureau of Standards.

<sup>3</sup> *J. Inst. Petroleum Tech.*, **10**, 914 (1924).

<sup>4</sup> *Proc. Am. Soc. Testing Materials*, **25**, 269 (1925).

flame is removed from under the absorber, the solution in which is then titrated as in Method D-90-26T. For more accurate work it is titrated until its color matches that in a similar absorber in which 10 cc. of standard sodium carbonate, 10 cc. of standard hydrochloric acid, and sufficient methyl orange have been mixed. One cubic centimeter of each solution is equivalent to 1 mg. of sulfur, and the same amount of methyl orange is present in each absorber.

Since the volume of sample burned is always 5 cc., the weight burned may be calculated from the specific gravity. For most unblended fuels only a small error is introduced if the figure 3.75 is assumed as the weight burned. The sulfur content may be expressed on a volume basis—i. e., as milligrams per liter, or grains per gallon—without measuring or assuming a value for the specific gravity.

As soon as the fuel has completely run out of the reservoir, another run may be started. It is unnecessary to rinse or clean the apparatus.

When working with very volatile fuels, it is sometimes advisable to decrease the heating current by connecting an auxiliary resistance in series. This is necessary, however, only in the rare case that a fuel boils in the reservoir when the full heat is maintained. It is also sometimes necessary, with such fuel or fuels containing dissolved gases, to place a few threads of glass wool in the tube leading from the fuel regulator to the vaporization chamber, so that bubbles of vapor forming there will not interfere with the smooth operation of the burner. As these threads cause no inconvenience when working with other fuels, they may be left in place permanently.

Variation of the size of flame has little, if any, effect on the results. It is convenient, however, to adjust the air and fuel regulators so that the flame is initially about  $\frac{1}{2}$  inch (13 mm.) high and colorless or slightly yellow at the tip of the inner cone. This flame is steady and does not overheat the glass chimney. As the fuel is burned nearly four times as fast in this method as in Method D-90-26T, it is necessary to increase the suction on the absorber to accommodate the larger amount of products of combustion.

#### Advantages of Method

(1) Accurate determination of sulfur, either elementary or in any form of combination which occurs in motor fuels, naphthas, and similar products.

(2) Precision. The average deviation, based on two runs on each of fifty samples containing from 0.04 to 0.17 per cent by the same operator was 0.0013 per cent of sulfur. The average deviation for different operators, based on available data of Sub-Committee VII, is 0.0034 per cent of sulfur, as compared with 0.0142 per cent when the same samples were tested by the same operators using Method D-90-26T. Further data are being obtained.

(3) Rapidity. The average time consumed in making one run by the new method is 45 minutes. This is less than half the time consumed by any other method. As practically no attention need be paid to the apparatus between the times of starting and titrating, a large number of tests may be run simultaneously, or other work may be attended to while the test is proceeding.

## Vitamins in Canned Foods<sup>1</sup>

### VI—Strawberries

E. F. Kohman, W. H. Eddy, and Nellie Halliday

NATIONAL CANNERS ASSOCIATION, WASHINGTON, D. C., AND TEACHERS COLLEGE, COLUMBIA UNIVERSITY, NEW YORK, N. Y.

IN THE previous papers of this series<sup>2</sup> it has been amply demonstrated that the major factor in destruction of vitamin C in cooking and canning of foods is oxidation. In fact, it has been shown that in canning, after a certain amount of preliminary destruction, subsequent heating has very little effect in the way of further destruction. In the canning of tomatoes there is either no preliminary destruction or it is of such small magnitude that it has not yet been demonstrated. With apples and peaches it was shown that after a preliminary treatment of these fruits, in which their respiratory process was utilized to deplete their oxygen supply and any intermediary respiratory oxygen, if such exists, then canning could proceed with no demonstrable loss of vitamin C. These results indicate that if vitamin C were heated in a suitable medium entirely free from oxidative factors, it would be unaffected by temperatures met with by canning or cooking. Silva<sup>3</sup> subjected the highly potent concentration of vitamin C obtained from lemon juice to a temperature of 140° C. for several hours in an oxygen-free atmosphere, and under those conditions could not demonstrate any destruction in potency.

Little is known about the detailed mechanism of the respiratory process in vegetable tissue whereby oxygen is consumed and carbon dioxide evolved. Analogy, however, strongly

suggests that there must be an intermediary form of respiratory oxygen and that this might exert an oxidative effect on vitamin C. This experiment with strawberries was planned with the hope that some such effect might manifest itself unless the process of "exhausting" in commercial canning was adequate to nullify any such effect.

It is known that when fruits are held at a low temperature and then transferred to a warmer temperature the evolution of carbon dioxide is more rapid for some time than it would be if held continuously at that particular temperature. This may be explained in part by the fact that the oxygen content of the gas in fruits is higher in cold storage owing to the inhibition of oxygen consumption. It is held by some to mean that during this period in cold storage the fruits accumulate intermediary respiratory oxygen, which when transferred to a warmer temperature gives rise to a more rapid formation of the carbon dioxide. In the exhaust box used in canning, fruits, with their oxygen supply cut off by the sirup surrounding them, are gradually warmed to above the temperature at which enzymes cease to function. Before this is reached the respiratory processes are greatly accelerated, and if the time before this is reached is adequate, all available oxygen is consumed.

It would be desirable to know the approximate vitamin content of all food products and how this is affected by the conditions that each meets with during distribution and preparation for consumption. The laborious methods of

<sup>1</sup> Received November 11, 1927.

<sup>2</sup> *Ind. Eng. Chem.*, **16**, 52, 1261 (1924); **17**, 69 (1925); **18**, 85, 302 (1926).

<sup>3</sup> Private communication to one of the authors.

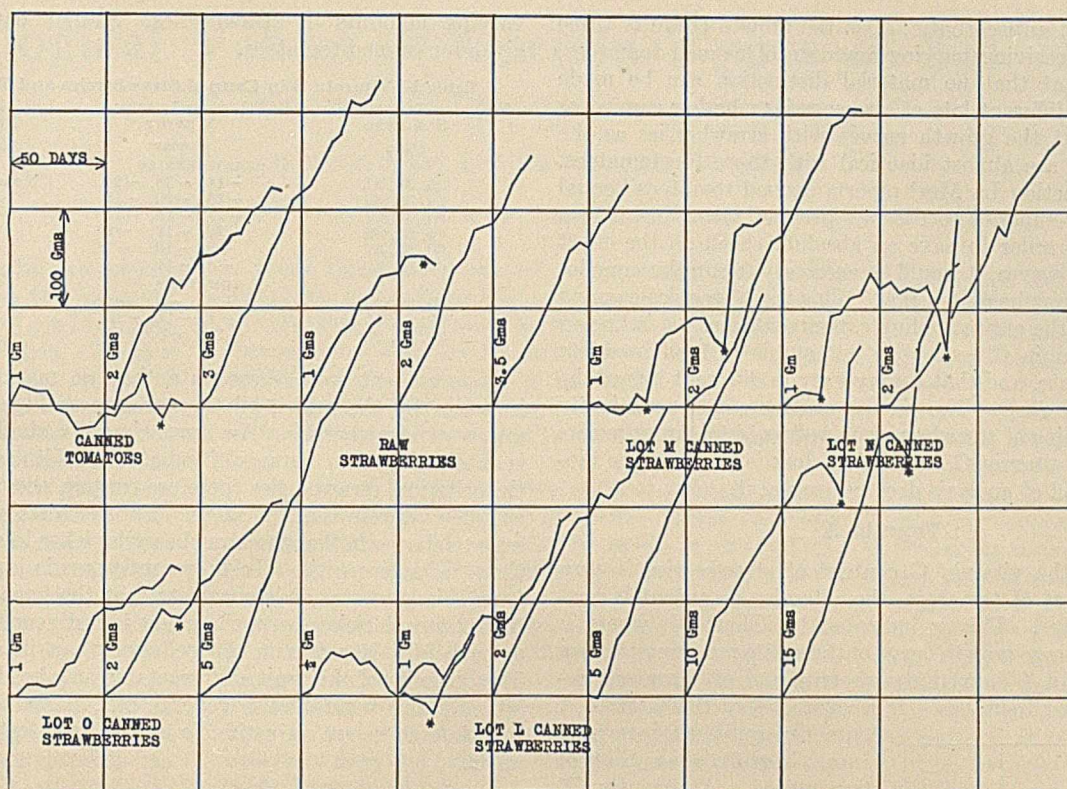


Chart I—Average Growth Curves of Three Guinea Pigs Receiving Varying Amounts of Canned Tomatoes, Raw Strawberries, and Canned Strawberries as a Source of Vitamin C

\* Indicates one of the animals died and from then on the curve is the average growth curve of the remaining animals.

determining vitamins will deny the fulfilment of this desire for a long time to come, and we must still content ourselves with conclusions by analogy. With this in mind an attempt has been made in this series of studies to select foods representative of various types. For this reason the data on strawberries presented herewith are of particular interest since information pertaining to vitamins in berries is almost negligible. The only data found pertaining to strawberries are those recorded by Smith, Berghem, and Hawk,<sup>4</sup> who state that 10 cc. of strawberry juice, raw or boiled, cured guinea pigs of scurvy in 7 days.

#### Experimental

Four lots of strawberries were canned on May 28, 1926, in Oregon, all of one variety, grown in the same field. They arrived at the receiving porch about 3:00 P. M., May 27, when they were divided into the following four lots:

**Lot L.** The strawberries were held on the receiving porch overnight until noon the next day to be canned concurrently with the other three lots when they were ready. The temperature was relatively low, the minimum temperature during the night being 50° F. This lot represents commercial practice and about the maximum time strawberries are held in the receiving room before canning.

**Lot M.** At 5:00 P. M. on the evening of May 27 the berries were transferred to a warm room of temperature 75° F., and held there until noon the following day.

**Lot N.** The berries were put in an ice box at 34° F. at 4:30 P. M. on the evening of May 27 and held there until noon of the following day.

**Lot O.** The berries were put in an ice box at 34° F. at 4:30 P. M., May 27, and held there until 9:00 A. M. on the following morning, when they were transferred to a warm atmosphere over steam boilers where the temperature was approximately 90° F. They were held under these conditions for 3 hours and 40 minutes.

At 12:30 P. M. on May 28 the four lots were stemmed and filled into cans in alphabetical order, each lot requiring

approximately 15 minutes. An average of 360 grams of strawberries was filled into No. 2 cans. The cans were then filled with water which had been boiled and then cooled to 120° F. The open cans were then passed through the steam exhaust box, which was held at 190° F. and which required 12 minutes. After this the cans were closed and cooked in boiling water for 8 minutes and then cooled in cold water.

The purpose of holding lot *N* in cold storage during the entire period up to the time of canning was to permit the berries to accumulate oxygen in any available form. The purpose of holding lot *M* at relatively high temperature was to avoid the accumulation of any intermediary respiratory oxygen and lower the gaseous oxygen content as far as possible. The purpose of transferring lot *O* from cold storage to a relatively warm temperature was to add to the effect of the exhaust in the event of its proving inadequate in eliminating the effect of gaseous oxygen or any intermediary respiratory oxygen. Lot *L* represents the regular commercial practice of canning strawberries and may be considered as occupying a place in between lots *M* and *N*.

The canned berries were all shipped to the laboratory at Teachers College and held until there was opportunity for determining the vitamin content, which was during the months of July, August, September, and October of 1927—i. e., approximately one and one-fourth years after canning. In the meantime, during May, June, July, and August, 1927, raw strawberries were purchased daily on the New York markets and fed in the raw state in comparison with those that were canned. It was not considered that vitamins A and B would be appreciably affected by the canning process and therefore these vitamins were determined only for lot *L* of the canned strawberries.

#### Results

Chart I gives the average growth curves of three guinea pigs receiving varying amounts of berries from each lot as the

<sup>4</sup> *Proc. Soc. Exptl. Biol. Med.*, 19, 228 (1921).

only source of antiscorbutic; also the growth curve of three guinea pigs receiving varying amounts of canned tomatoes.

It is evident that no material distinction can be made between the different lots of strawberries whether canned or raw, and that the growth curves with strawberries as the antiscorbutic are almost identical with those for tomatoes. In this connection La Mer<sup>5</sup> reports canned tomatoes "equal to or slightly superior to the raw product raised in his own garden." In order to have an absolute check on the effect of canning, however, it would be necessary to can the same lot of food that was being fed raw. This would require canning daily during the entire feeding experiment, since it is known that the vitamin C content is not stable in food products in the raw state, and that it may vary in different lots of the same kind of food. The results of this experiment imply that the canning of strawberries as well as of tomatoes results in no loss of vitamin C, or that the loss is so small the biological method of analysis does not reveal it.

### Vitamin A

Although the vitamin C content of strawberries is very similar to that of tomatoes, the vitamin A content is considerably lower. This is indicated by Chart II, where is given the average growth curve of three rats receiving varying amounts of lot L canned strawberries and of other rats receiving canned tomatoes. It is evident that the vitamin A

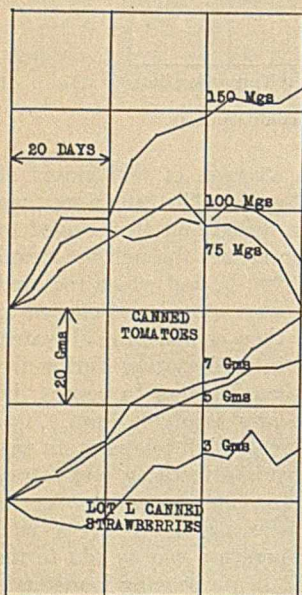


Chart II—Average Growth Curves of Three Rats Receiving Varying Amounts of Lot L Canned Strawberries and Canned Tomatoes as a Source of Vitamin A

content of tomatoes is several times higher than that of strawberries. Apparently 75 to 100 mg. of tomatoes is the equivalent of 3 grams of strawberries. This tends to emphasize the danger of estimating vitamin contents of foods by analogy and the necessity of determining it for each product. It was not deemed likely that the canning process would have any appreciable effect on vitamin A since it is more stable than vitamin C. Hence, only lot L of the canned strawberries was tested.

### Vitamin B

The situation in regard to vitamin B content of foods is very emphatically a quandary. It is now demonstrated<sup>6</sup> that what we have previously considered vitamin B is in reality at least two fractions. One of these (antineuritic) is much

more heat-labile than the other (antipellagric). The old technic for the determination of vitamin B gives us the amount of foodstuff which is necessary to meet the rat's requirement of both substances, but it does not differentiate between the amount of each factor. The data on vitamin B presented in this paper were obtained by the Sherman rat-growth technic.

In Table I under column 1 is given the number of days of the 60-day feeding test that each rat survived, while under column 2 is given gain or loss in weight of three rats receiving

varying amounts of strawberries. Similar data are also given for canned tomatoes.

Table I—Vitamin B in Canned Strawberries and Tomatoes

TIME SURVIVED Days	GAIN OR LOSS IN WEIGHT Grams	DAILY FEEDING Grams
29, 36, 31	-18, -38, -24	None (control)
29, 33, 30	-19, -20, -18	2
60, 36, 27	-17, -18, -12	4
44, 60, 39	-22, -17, -9	6
60, 60, 37	-8, -10, -1	8
60, 60, 60	-6, -11, +1	10
TOMATOES		
60, 60, 37	-8, -9, -5	2
60, 52, 56	-1, -12, -13	3
60, 60, 60	-17, +6, +21	5

It is evident from these data that no marked response is shown by the rats until they receive as high as 8 to 10 grams of strawberries. An approximately similar response is obtained by 2 to 3 grams of tomatoes. With rat growth as the criterion, strawberries therefore contain about one-fourth as much vitamin B as tomatoes. Further tests will be necessary to show whether the strawberry is richer in antipellagric than in antineuritic. Tests recently made and reported from this laboratory<sup>7</sup> demonstrate that the banana is nearly three times as rich in antipellagric as in antineuritic, and that spinach also is richer in antipellagric than in antineuritic. The behavior of this fruit and vegetable may be characteristic of fruits and vegetables in general, but, as stated elsewhere, such inferences are unjustifiable until actual tests have been made.

### Discussion

A word may well be said regarding the variation in animals used for such work. Examination of Chart I will reveal that all three pigs on 5 grams of lot L canned strawberries thrived while one each of the pigs receiving 10 and 15 grams died from some unknown cause before the 90-day period, the other two being normal in every respect. Even in the face of such variations, the evidence is ample to indicate that strawberries are an excellent source of vitamin C, equivalent in antiscorbutic properties to tomatoes and oranges. Furthermore, canning, even with a wider variation of conditions than is found in commercial practice, appears to have very little effect on vitamin C. Either oxidation is not a material factor or the process of exhausting employed in commercial canning nullifies it. Since strawberries contain gas approximately equivalent to 8 to 10 per cent of their volume, and this is normally around 10 per cent oxygen but higher under cold storage temperatures, it is believed that the exhaust plays an important role in this connection.

Although strawberries compare very favorably with tomatoes in vitamin C, they are only about one-fortieth as well supplied in vitamin A and one-fourth as rich in vitamin B.

### Conclusions

1—Strawberries are a rich source of vitamin C, similar to tomatoes in this respect. The daily feeding required for protection against scurvy and normal growth of the guinea pig is between 2 and 3 grams.

2—Commercially canned strawberries considerably over a year after canning have a similar vitamin C content to the raw strawberries.

3—Since strawberries contain considerable oxygen, it is indicated that the exhaust plays an important part in making it possible to can them with no apparent loss in vitamin C.

4—Strawberries are not highly endowed with vitamin A, being only one-fortieth as rich in it as tomatoes.

5—Strawberries are about one-fourth as rich in vitamin B as tomatoes.

<sup>7</sup> Eddy, *Proc. Soc. Exptl. Biol. Med.*, **25**, 125 (1927).

<sup>5</sup> Dissertation, Columbia University, 1921.

<sup>6</sup> Chick and Roscoe, *Biochem. J.*, **21**, 698 (1927); Smith and Hendrick, *U. S. Pub. Health Service, Pub. Health Rept.* **41**, 201 (1926); Goldberger and co-workers, *Ibid.*, **41**, 297, 1025 (1926); Hauge and Carrick, *J. Biol. Chem.*, **69**, 403 (1926); Salmon, *Ibid.*, **73**, 483 (1927); Williams and Waterman, *Proc. Soc. Exptl. Biol. Med.*, **25**, 1 (1927).

# Biological Values of Certain Types of Sea Food<sup>1</sup>

## II—Vitamins in Oysters (*Ostrea virginica*)<sup>2</sup>

D. Breese Jones, J. C. Murphy, and E. M. Nelson

PROTEIN AND NUTRITION DIVISION, BUREAU OF CHEMISTRY AND SOILS, WASHINGTON, D. C.

**F**EW data are available on the biological value of sea food, particularly shell fish. There is probably no class of food of equal importance that has received such scanty attention from the standpoint of its general nutritive properties. In former years shell fish were prized chiefly because of their delicate and appetizing flavor. Modern discoveries in the field of nutrition, particularly with reference to vitamins and to the part played by certain mineral constituents—as calcium, phosphorus, iodine, iron, and other elements—in their relation to such diseases as rickets, goiter, and anemia, suggest that oysters may have marked food values aside from their gustatory properties.

Oysters constitute the most valuable fishery product of the United States. The annual yield in this country is about 30 million bushels, with a return to the fishermen of nearly 15 million dollars.

This article is the second of a series of studies projected by the Protein and Nutrition Division of the Bureau of Chemistry and Soils on the biological properties of shell fish from the standpoint of their vitamin content and the nutritive quality of their proteins.<sup>2</sup>

The subject of vitamins in oysters has a twofold interest, as has been recently pointed out<sup>3</sup> in a general preliminary survey of the results of work done in this laboratory on the vitamins and proteins of oysters, clams, and shrimp. In the first place, oysters constitute an important and extensively used item of food; any additional information regarding their food value is therefore desirable. In the second place, the material upon which oysters feed consists largely of diatoms and minute organisms, marine forms of life to which have been traced<sup>4 to 7</sup> the origin of the fat-soluble vitamins found so abundantly in certain fish-liver oils, such as that of the cod. In a comprehensive review of work done by numerous investigators on the food of oysters, Sav-

Fresh Chesapeake oysters were ground in a frozen condition to a homogeneous consistency, and preserved in this state throughout the period of experimentation. Experiments with albino rats showed that oysters are a good source of vitamins A, B, and D.

Two grams (0.32 gram on a dry basis) of oysters furnished sufficient vitamin A to cure rats of xerophthalmia.

Tests made by the curative method showed that 3.5 grams (0.56 gram dry basis) of oysters contained nearly enough vitamin B to supply the needs of young rats. For long-continued normal growth, however, a little more than 5 grams (0.8 gram dry basis) was required.

Five grams of oysters given to rachitic rats daily for 10 days induced slight calcification of the long bones, comparable in degree with that produced in the same length of time by 4 mg. of good cod-liver oil. The same daily quantity of oysters induced about half calcification in 15 days and complete calcification of the rachitic metaphyses in 20 days.

Oysters were found deficient in the factor required for reproduction and rearing of young.

Dehydration at 40° C. under reduced pressure (10 to 15 mm.) was found to inactivate to a great extent vitamins A and B in oysters.

age<sup>8</sup> shows that in certain cases, depending on the season and locality, oysters live almost exclusively on diatoms.

But little work has been published heretofore on vitamins in oysters. Randoin<sup>9</sup> found that guinea pigs fed a vitamin C-deficient diet supplemented with 15 grams of oysters daily maintained their weight for 6 weeks and did not develop scurvy. Later Malcolm,<sup>10</sup> working with ethereal extracts of oysters, was unable to detect the presence of any vitamin A.

The oysters used in the work described herein were fresh, medium-sized, Chesapeake oysters purchased on the Washington market. They were obtained for the greater part during the winter. For reasons hereinafter

stated, the oysters were frozen as soon as possible, ground, and kept in the frozen condition during the periods of experimentation. Estimation of vitamins A, B, and D in the frozen oysters, made by means of feeding tests with albino rats, showed that, on a dry basis, the oysters used contained these vitamins in proportions that compare favorably with those of other foods that are highly regarded as sources of these dietary accessory factors.

During the course of the work some evidence was obtained suggesting that there may be a seasonal variation in the vitamin content of oysters. This phase of the subject is now under investigation.

It was found that fresh oysters dehydrated at a low temperature under reduced atmospheric pressure had lost nearly all their original vitamin B properties and a very significant proportion of those of vitamin A. This loss of vitamin properties during dehydration was attended by other changes of a chemical nature. The possible reasons for the destruction of these vitamins under such mild treatment are discussed elsewhere.

### Vitamin B

**CURATIVE METHOD**—In the curative tests for vitamin B young albino rats weighing from 45 to 55 grams were fed the vitamin B-free basal ration indicated on the charts. When a decided decline in the weight of the animals had occurred as a result of vitamin B deficiency in the diet, the material to be tested, with one or two exceptions, was fed at definite levels daily apart from the basal ration. Osborne

<sup>1</sup> Received September 14, 1927. A preliminary report of this work, which was started in the fall of 1924, was read at the meeting of the Society for Experimental Biology and Medicine held in New York, April, 1926. An abstract of this paper was later published in *Proc. Soc. Exptl. Biol. Med.*, **23**, 519 (1926).

<sup>2</sup> The first article of this series was published under the title "Nitrogen Distribution and Percentages of Some Amino Acids in the Muscle of the Shrimp, *Peneus setiferus* (L.)," Jones, Moeller, and Gersdorff, *J. Biol. Chem.*, **65**, 59 (1925).

<sup>3</sup> Jones, *Am. J. Pub. Health*, **16**, 1177 (1926).

<sup>4</sup> Hjort, *Proc. Roy. Soc. (London)*, **B93**, 440 (1922).

<sup>5</sup> Coward and Drummond, *Biochem. J.*, **15**, 530 (1921).

<sup>6</sup> Jameson, Coward, and Drummond, *Ibid.*, **16**, 482 (1922).

<sup>7</sup> Drummond and Zilva, *Ibid.*, **16**, 518 (1922).

<sup>8</sup> Fishery Investigations, Series II, H. M. Stationery Office, London, **8**, No. 1 (1925).

<sup>9</sup> *Compt. rend.*, **177**, 498 (1923).

<sup>10</sup> *Trans. Proc. New Zealand Inst.*, **56**, 650 (1926).

and Mendel's salt mixture was used in all the diets except the rachitic diet. The rats were kept in cages having raised screen bottoms to prevent them from having access to their excreta.

**Dehydrated Oysters.** In the first experiments a product prepared by dehydrating fresh oysters at a temperature not exceeding 40–45° C., and at 10 to 15 mm. atmospheric pressure, was used. This usually required about 30 hours. The product was dark colored, and its odor and general properties indicated that during the process of dehydration chemical changes had taken place. The dry residue was ground to a powder. When this product was fed, separate from the basal diet, difficulty was encountered in getting many of the rats to eat all the daily portions allotted to them. The dehydrated oysters were fed in daily doses of 0.25 and 0.5 gram. As can be seen from the growth curves in Chart I, 0.25 gram merely retarded, but did not arrest, the decline in weight of the animals. Fed at a daily level of 0.5 gram, the weight decline was arrested, followed by a slow growth for about 2 weeks with subsequent loss of weight.

Another lot of rats was fed the oyster meal incorporated in the basal diet at a 7 per cent level. Based on their average food consumption, this quantity of oysters in the diet furnished approximately a daily intake of 0.5 gram of dehydrated oysters. The results, as shown on Chart I, indicate the presence of but little vitamin B. The quantities of the dehydrated product fed, 0.25 and 0.5 gram, represent 1.5 and 3.1 grams, respectively, of fresh oysters. Compared with the results obtained later (Charts II and III) with fresh, frozen oysters, the vitamin B content of the dehydrated product was decidedly less than that of the fresh oysters, indicating that during the process of dehydration there was some destruction of vitamin B.

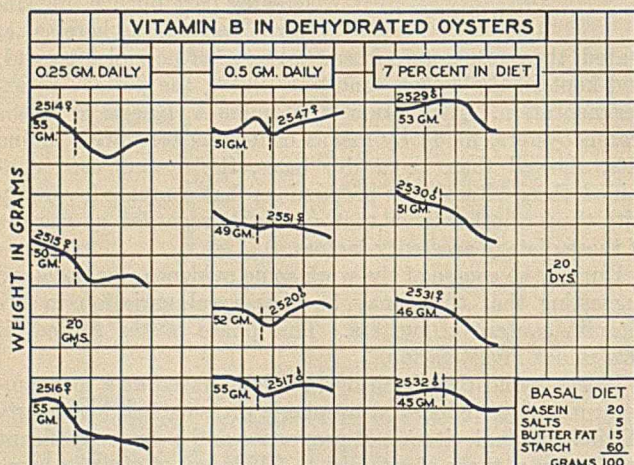


Chart I

**Raw, Frozen Oysters.** On account of changes that took place in the oysters during dehydration and the apparent injurious effect upon vitamin B, it became necessary, in order to get data from which the vitamin B content of fresh oysters could be fairly evaluated, to devise a method which, without impairment of the vitamin, would yield a palatable product having uniform composition, and which could both be kept without deterioration throughout the period of experimentation and be satisfactorily weighed out in the desired quantities for the daily feeding. This was accomplished by separating the liquor from the fresh oysters as far as possible by draining in cheesecloth, and placing the oyster meats in a cold-storage room at a temperature below freezing. The frozen product was then finely ground in a meat grinder which had been cooled to the temperature of the freezing

room. In this way a homogeneous product was obtained of which uniform samples could be weighed. It has been previously shown that freezing temperatures have no appreciable effect on vitamins.<sup>11</sup> The rats eagerly ate the quantities of the frozen oysters that were daily allotted to them.

Estimations of the vitamin B content of the frozen oysters were made both by the curative and by the prophylactic methods. In the experiments made by the curative method, different lots of rats, after having been fed the vitamin B-

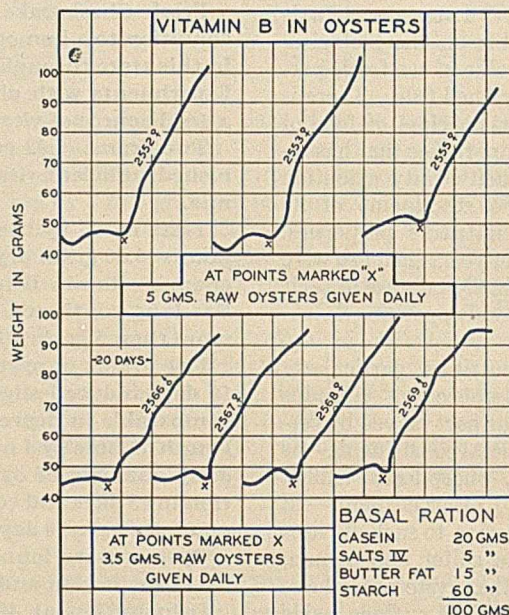


Chart II

free basal ration until a marked decline in weight had resulted, were given the oysters daily in quantities of 1, 2, 3.5, and 5 grams. The results are presented in Charts II and III. In all cases the decline in weight attending the preliminary period was promptly arrested. With 5 grams of oysters growth followed at an excellent and uniform rate for 4 weeks. Growth at a somewhat slower rate resulted with the 3.5-gram portions, whereas with 2 grams of oysters daily the animals grew at a fair rate for about 3 or 4 weeks, with a tendency to decline in weight thereafter. A slow rate of growth for 2 or 3 weeks followed the administration of 1 gram of oyster, followed by a decided decline in weight.

These results indicate that 3.5 grams of oysters daily are nearly sufficient to provide the quantity of vitamin B necessary for the normal growth of young rats.

**PROPHYLACTIC METHOD**—Although results obtained with young animals by the curative method give a fair idea of the vitamin content of the substance under examination, this method does not allow so rigorous a test as does the prophylactic method continued over a much longer period of time and covering most of the growing stage of the animal. A quantity of substance that would furnish enough vitamin to stimulate a young animal's recovery from vitamin starvation, and to grow thereafter at an excellent rate for 3 or 4 weeks, may not be adequate to supply the animal's need throughout the greater part of its normal growth period.

In order to check the results obtained by the curative method, four lots of young rats weighing from 45 to 50 grams were fed the basal diet supplemented by 1, 2, 3.5, and 5 grams of frozen oysters daily.

The results of these tests are shown in Charts IV, V, and VI. One gram daily enabled the animals to do but little better than the controls on the vitamin B-free diet. With

<sup>11</sup> Jones, Murphy, and Moeller, *Am. J. Physiol.*, **71**, 265 (1925).



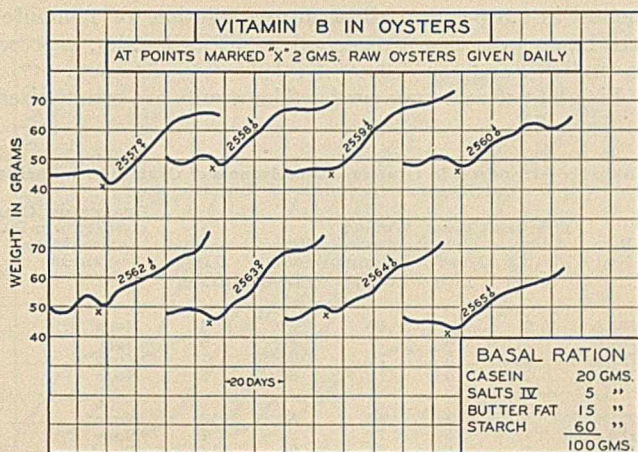


Chart III

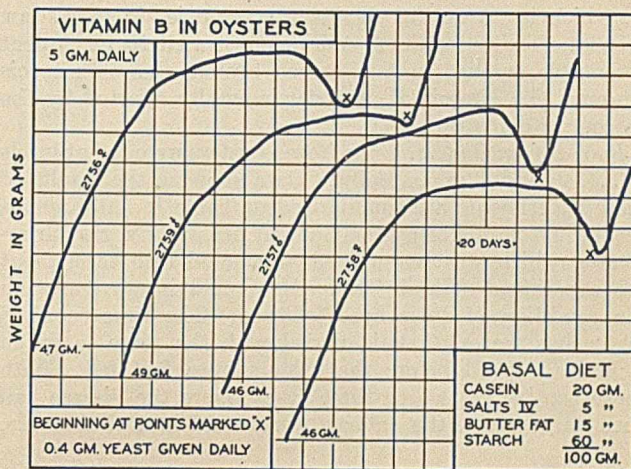


Chart IV

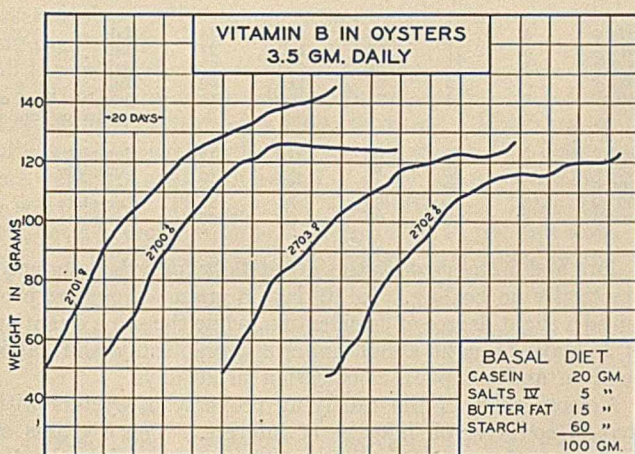


Chart V

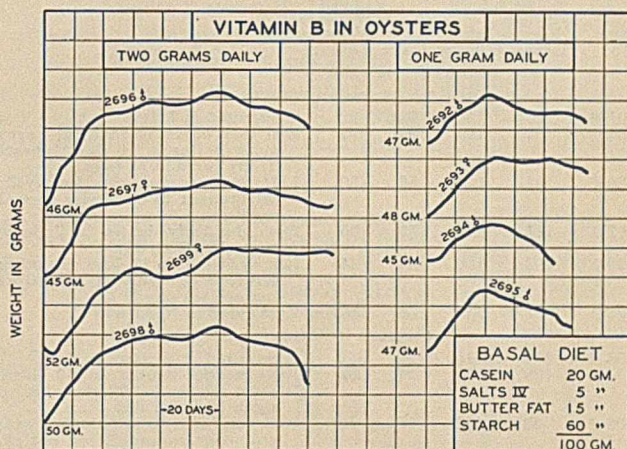


Chart VI

2 grams a slow rate of growth for about 60 days resulted, followed by a decline. Growth at a satisfactory rate for about 9 weeks attended the administration of 3.5 grams of oysters. After that the rate of growth was more or less retarded.

It is of interest to note that as tested by the curative method (Chart II), 5 grams of oysters daily appeared to supply sufficient vitamin B to meet growth requirements of young rats. Tested by the prophylactic method, however (Chart IV), the same quantity of oysters, although enabling the animals to grow at an excellent rate for about 60 days, yet failed to maintain growth at that rate for a longer period. After about 12 weeks the animals suffered a rapid decline in weight. That this decline was caused by an insufficient amount of vitamin B was shown by the prompt resumption of growth following substitution of 0.4 gram of yeast<sup>12</sup> daily for the 5 grams of oysters. A comparison of the results obtained by the curative and the prophylactic methods shows that the latter method disclosed a degree of vitamin deficiency that could not have been detected by the results obtained by the curative method.

The frozen oysters used in these experiments contained 84 per cent of water. The various quantities fed—namely, 1, 2, 3.5, and 5 grams—therefore represent 0.16, 0.32, 0.56, and 0.80 gram, respectively, of dry material. On this basis oysters compare favorably as a source of vitamin B with foods which are recognized as excellent sources of this dietary factor.

<sup>12</sup> The yeast used in these experiments was furnished by the Northwestern Yeast Company, through the courtesy of M. H. Givens.

In view of the apparent ease with which vitamin B was destroyed during the process of dehydration, the effects of cooking upon the vitamin B content of oysters was studied. A lot of fresh oysters was divided into two portions. One portion was immediately frozen, and the other was heated for about 2 hours in closed glass jars in boiling water. The cooked portion was then frozen. Estimation of the vitamin B content of both portions carried out in parallel feeding tests with 2 grams of the oysters daily showed that the cooking had produced a small decrease in the vitamin content of the oysters.

#### Vitamin A

The estimation of vitamin A was carried out by the curative method. Young rats were fed the vitamin A-free basal ration indicated on the charts until well-developed symptoms of xerophthalmia had resulted. Portions of the material to be tested were than given daily, and the effect on the condition of the eyes was noted. Vitamin B was supplied daily by 0.4 gram of yeast, given in the form of tablets, prepared in the laboratory.

*Dehydrated Oysters.* Experiments with dehydrated oysters fed daily in quantities of 0.25 and 0.5 gram indicated the presence of little or no vitamin A. In practically all cases where the portions fed were eaten there was a definite growth response, which continued at a fair rate for 30 days or longer. There was, however, no noticeable improvement in the ophthalmic condition of the animals. The temporary growth response noted is probably to be ascribed to the growth-promoting property of the more stable vitamin

D, which is present in significant quantities in fresh, raw oysters. That vitamin A was demonstrated to be present in notable amount in raw, frozen oysters shows that this vitamin, like vitamin B, was detrimentally affected by the process of dehydration.

*Raw, Frozen Oysters.* The frozen oysters were fed at levels of 3.5, 2, and 1 grams daily. Data showing the results of these experiments are summarized in Table I. All animals getting 3.5 grams of oysters showed promptly a growth response, which was maintained at a good rate throughout the experiment (Chart VII). Also rapid improvement in the condition of their eyes followed. The time required for curing the ophthalmia varied with the stage to which it had advanced before the oysters were first fed. With the exception of two or three cases where the disease had been very severe, the animals were cured in 1 to 2 weeks.

Table I—Vitamin A in Oysters—Effectiveness of Oysters in Curing Xerophthalmia in Rats

RAT NO.	WEIGHT WHEN OYSTERS GIVEN		TIME OYSTERS WERE GIVEN		REMARKS
	First Given Grams	Final Weight Grams	Days	Days	
3.5 GRAMS OYSTERS DAILY					
2601 ♂	78	150	72	30	Eyes cured in 7 days
2588 ♂	81	135	54	29	Bad case of xerophthalmia; eyes much better in 10 days; practically cured in 14 days
2589 ♂	94	152	58	30	Left eye permanently destroyed; rat brought to otherwise normal condition
2597 ♀	111	150	39	35	Eyes decidedly better in 7 days; normal by 30th day
2599 ♀	105	159	54	48	Left eye cured in 17 days, the other slowly improved and normal at end of 35th day
2586 ♀	82	137	55	36	Eyes cured in 10 days
2 GRAMS OYSTERS DAILY					
2598 ♂	115	145	30	32	Eyes cured in 18 days
2595 ♂	109	133	24	32	Eyes nearly normal in 10 days; slight relapse on 20th day; healed again by 30th day
2603 ♂	83	148	65	49	Bad case of xerophthalmia; eyes gradually improved, but not entirely cured at end of experiment
2670 ♀	94	133	39	35	Eyes cured in 10 days
2605 ♂	77	117	40	30	Eyes cured in 18 days
1 GRAM OYSTERS DAILY					
2736 ♀	93	116	23	39	No improvement in condition of eyes
2740 ♀	75	65	-10	32	Xerophthalmia gradually became worse

Two-gram daily portions of the oysters also caused a prompt growth response (Chart VIII), although at a slower rate than when 3.5 grams were fed. That this quantity of oysters contained enough vitamin A to cure rats of xerophthalmia is shown in Table I. Cures resulted in all the rats in this lot, excepting in rat 2603, where the disease had progressed to such a degree before the oyster was fed that the animal's eyes had been irreparably damaged.

One gram of oysters had but little effect on growth, and showed no demonstrable curative effect on xerophthalmic rats.

### Vitamin D

Estimations of the antirachitic property of oysters were made by means of the so-called "line test" method.<sup>13</sup> Young rats weighing 60 to 70 grams were taken from their mothers and fed Steenbock's rachitic ration 2965,<sup>14, 15</sup> which consists of yellow corn, 76 parts; wheat gluten, 20 parts; calcium carbonate, 3 parts; and sodium chloride, 1 part. On this diet the writers' rats almost invariably develop severe rickets in about 3 weeks. At the end of this time the rats were given weighed portions of oysters daily for a definite number of days. The animals were then killed, their radii and ulnae split and im-

mersed in 0.5 per cent silver nitrate solution for 1 minute. The bones were then transferred to distilled water, exposed to sunlight, and the degree of calcification observed.

Five lots of rats were used. The results are summarized in Table II.

Table II—Vitamin D in Oysters—Effectiveness of Oysters in Inducing Calcification in Bones of Rachitic Rats

RAT NO.	OYSTERS GIVEN DAILY Grams	TIME GIVEN OYSTERS Days	WEIGHT WHEN CHANGED Grams	FINAL WEIGHT Grams	GAIN Grams	DEGREE OF CALCIFICATION OF RACHITIC METAPHYSES
LOT I						
2763 ♀	2	5	69	77	8	None
2764 ♂	2	5	77	86	9	None
2765 ♀	2	5	71	78	7	None
2768 ♂	2	5	79	86	7	None
LOT II						
2788 ♀	5	5	69	82	13	None
2789 ♂	5	5	77	84	7	None
2790 ♂	5	5	81	95	14	Slight
2791 ♂	5	5	80	84	4	None
LOT III						
2802 ♂	5	10	84	113	29	Slight
LOT IV						
2870 ♀	5	15	75	108	33	Half
2871 ♂	5	15	83	110	27	Half
2872 ♀	5	15	73	95	22	Half
2873 ♂	5	15	95	115	20	Half
2803 ♂	5	15	77	95	18	Definite line of calcification
LOT V						
2808 ♀	5	20	91	110	19	Complete
2809 ♀	5	20	87	104	17	Complete
2900 ♀	5	20	68	86	18	Complete
2901 ♀	5	20	60	81	21	Complete
2902 ♀	5	20	67	96	29	Complete

Two and 5 grams of oysters given daily for 5 days induced practically no healing. In 10 days 5 grams of oysters produced a slight degree of calcification, while the same quantity in 15 days brought about uniformly practically half calcification, and complete calcification in 20 days.

A comparison of the calcifying property of oysters with that of cod-liver oil may be of interest. The 5 grams of oysters used represent 800 mg. of dry material. Under similar conditions approximately the same degree of calcification is brought about by 4 mg. of a good grade of cod-liver oil, or  $\frac{1}{200}$  of the quantity of oysters required. Oysters contain about 1.3 per cent of fat. Comparing the antirachitic value of oysters with that of cod-liver oil on a fat basis, and assuming for the sake of comparison that all of vitamin D in the oyster is resident in the fat, we find that 65 mg. of oyster fat is antirachitically equivalent to 4 mg. of cod-liver oil.

### Reproduction and Rearing of Young

Ground, dried oysters incorporated in the basal diet were used in these experiments. The oysters were prepared by pouring fresh oysters, together with their liquor, into boiling water in a steam-jacketed kettle. After boiling for 4 minutes the oysters were drained through two thicknesses of cheesecloth and coarsely ground in a meat chopper. The product was then extracted three times with boiling water, drained, dried in a current of air at 70–80° C., and finally ground in a mill to a powder. Thus prepared, the product contained about 11 per cent of nitrogen.

Normal, healthy young rats from the stock colony, about 4 weeks old and weighing 50 to 60 grams, were grouped in two cages. Each cage contained 5 females and 2 males. The animals were then given a diet having the following composition: oyster meal, 26 parts; salt mixture, 5 parts; Crisco, 20 parts; and cornstarch, 49 parts. Cod-liver oil (4.3 parts) and yeast (5.7 parts) were incorporated in the diet to furnish vitamins A, B, and D. Pregnant rats were removed from the others and put into individual cages. The young were allowed to remain with their mothers until they weighed 40 to 50 grams and it was certain that they could

<sup>13</sup> McCollum, Simmonds, Shipley, and Park, *J. Biol. Chem.*, **51**, 41, (1922).

<sup>14</sup> Steenbock and Black, *Ibid.*, **64**, 263 (1925).

<sup>15</sup> Nelson and Steenbock, *Ibid.*, **64**, 299 (1925).

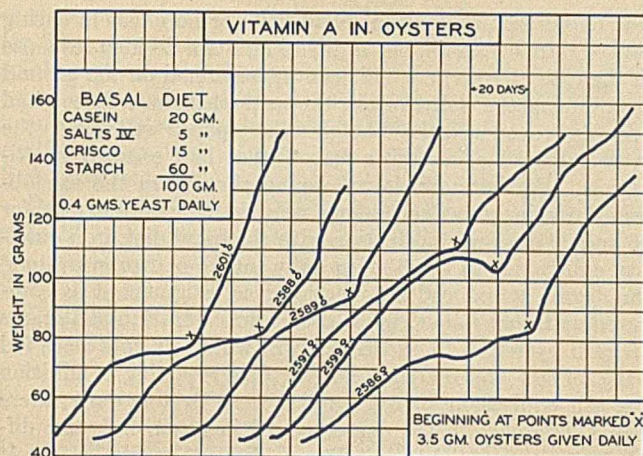


Chart VII

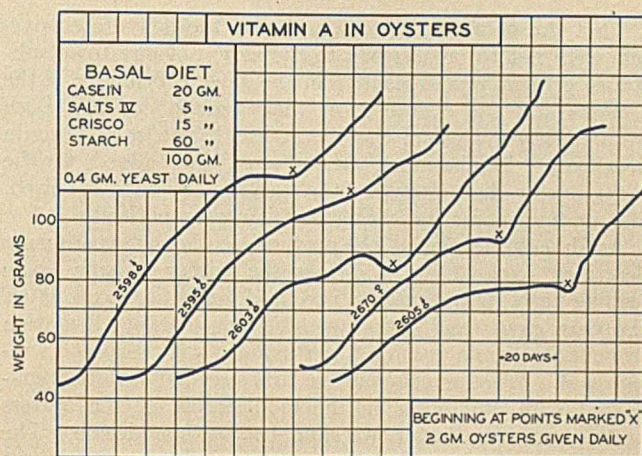


Chart VIII

be reared alone. The mothers were then returned to the group cages.

All the rats grew at a fairly satisfactory rate on this diet. The five females in group I had 24 litters, comprising a total of 124 young, of which only 23 were reared. Much poorer results were obtained with the rats in group II. Only 7 litters were produced with a total of 47 young, of which only one was reared. The data are summarized in Table III. Of the total young born in both groups only 14 per cent were reared. A large percentage of the others was eaten by the mothers.

Table III—Effect of Twenty-Six Parts of Oyster Meal in Diet upon Reproduction and Rearing of Young in First-Generation Rats

RAT No.	INITIAL WEIGHT Grams	TIME ON DIET Days	FINAL WEIGHT Grams	WEIGHT WHEN FIRST LITTER WAS BORN Grams	TOTAL NUMBER OF LITTERS	TOTAL YOUNG BORN	TOTAL YOUNG REARED	
GROUP I								
2774♂	65	245	320					
2775♂	75	245	267					
2776♀	45	245	245	187	4	12	6	
2777♀	55	273	203	188	6	25	4	
2778♀	52	245	228	220	6	39	0	
2779♀	60	270	216	169	4	24	4	
2780♀	50	245	163	191	4	24	9	
GROUP II								
2781♂	58	201	211					
2782♂	53	201	270					
2783♀	57	111	196	215	1	12	0	
2784♀	51	111	189	157	2	6	0	
2785♀	59	111	162	192	1	6	1	
2786♀	61	111	201	220	1	9	0	
2787♀	49	111	178	191	2	14	0	
					Total	31	171	24

The rats of the second generation on the oyster diet were practically infertile. A group consisting of 6 females and 2 males selected from the best of those reared by the first generation rats were removed from their mothers. The males and females were kept in separate cages until they were 10 to 11 weeks old. During the subsequent 19 weeks they were together, only two rats had young. Each had one litter of three, all of which were eaten by the mothers. A summary of the data is given in Table IV.

In order to ascertain whether the infertility of the second generation rats was to be ascribed to the males or to the females, or to both, the females were mated with 2 stock males of known previous fertility. During the following period of 2 weeks, three of the females had one litter each, with a total of 13 young; one female became pregnant, but no young were seen. Later she gave birth to a litter of 3, which was eaten. The other two females did not become pregnant. The 2 males that had been on the oyster diet were also mated to 5 stock females of known previous fer-

tility. The results were entirely negative. At the end of the experiment the males were killed and autopsied. The internal organs of the rats appeared normal with the exception that the testes were undersized. Each testicle of both rats weighed only 0.5 gram. For comparison the testicles of a stock rat 85 days old were examined and found to weigh 1.4 gram each.

Table IV—Effect of Twenty-Six Parts of Oyster Meal in Diet upon Reproduction and Rearing of Young in Second-Generation Rats

RAT No.	AGE WHEN MATED Days	WEIGHT WHEN MATED Grams	FINAL WEIGHT Grams	NUMBER OF LITTERS	TOTAL NUMBER OF YOUNG	TOTAL YOUNG REARED	
2903♂	82	172	228				
2904♂	71	140	278				
2905♀	82	150	196	1	3	0	
2906♀	67	80	190	0	0	0	
2907♀	67	121	218	0	0	0	
2909♀	67	88	178	0	0	0	
2910♀	67	97	191	1	3	0	
2911♀	67	98	197	0	0	0	
				Total	2	6	0

## Discussion

The apparent ease with which vitamins A and B were largely destroyed or inactivated during the process of dehydration is worthy of special mention. Under ordinary conditions these vitamins would not be seriously affected by heating them to about 40° C. in a vessel from which most of the air had been exhausted (10 to 15 mm. pressure). The cause for this change must therefore be ascribed to other influence than that of heat or ordinary atmospheric oxidation. The following explanations are suggested.

1—During the process of dehydration, which usually required about 30 hours, bacterial or enzymic action may have occurred which brought about the destruction or inactivation of the vitamins. The temperature at which the distillation was conducted (40° C.) was favorable for such a development. Attention has been directed<sup>16</sup> to the presence in fruit juices of oxidases which have a destructive effect on the vitamins.

2—It has been shown that traces of certain metallic elements, such as copper, have a destructive effect upon vitamins.<sup>17</sup> Addition of traces of certain metals to compounds that are easily oxidized accelerates both aerobic and anaerobic oxidation. Iron has been found to act as a peroxidase.<sup>18</sup> Oysters contain relatively large quantities of several metallic elements,<sup>19</sup> notably copper, lead, arsenic, and zinc. In view of the conditions under which the oysters were dehydrated it is not inconceivable that the deleterious effect upon the vitamins was due to the action of one or more of the metallic constituents of the oysters.

<sup>16</sup> Sucharipa, *Konserven-Ind.*, **12**, 623 (1925); *Chem. Zentr.*, **97** (I), 1594 (1926).

<sup>17</sup> Van Leersum, *J. Hygiene*, **25**, 461 (1926).

<sup>18</sup> Harrison, *Biochem. J.*, **21**, 335 (1927).

<sup>19</sup> U. S. Dept. Agr., *Food Drug Rev.*, **2**, No. 5, 27 (1927).

That the poor results obtained with the dehydrated oysters were not to be ascribed to the action of any toxic substance present was evident from the general behavior of the animals and the character of their growth curves. Both were strictly typical of the characteristic results of vitamin deficiency. Furthermore, when yeast was added to the same oyster diet, growth at a satisfactory rate followed, and no symptoms indicating toxicity were noticed.

As already mentioned, the oysters used in the experiments described were obtained during the winter. Later, some feeding tests with oysters procured at other seasons of the year gave results that showed considerable deviation from those herein recorded, particularly with respect to vitamin B. Whether this was due to a seasonal variation connected with differences in the food supply of the oysters or to some other factor, we cannot at present decide. The fact that the food supply of oysters greatly varies at different times of the year lends support to the former view.

In the tests in which rachitic rats fed the low phosphorus-high calcium diet were given daily 5 grams of frozen oysters, equivalent to 0.8 gram of dry material, approximately half calcification was induced in 15 days, and complete calcification in 20 days. Since oysters contain a significant amount of phosphorus, it might be contended that the calcifying property of oysters as found in these tests could be attributed, not to the presence of vitamin D, but to the superimposed phosphorus contained in the oysters fed. That this was not the case is shown in the following considerations. Oysters also contain considerable calcium, which would proportionally counterbalance any curative effect the phosphorus in the oysters might have. The general effect would be to continue to maintain a low phosphorus-high calcium ratio. In the vitamin A experiments with dehydrated oysters it

was found that this product had little or no effect in curing rats of xerophthalmia, but it did stimulate a decided response in the rate of growth. This can be explained on the ground that during the dehydration the antiophthalmic factor had been destroyed and that the growth response was due to the more resistant antirachitic factor, that had escaped inactivation. Furthermore, it was found that when the ash obtained by incinerating oysters was fed to rachitic rats for 15 and 20 days in conjunction with the basal diet, in a quantity equivalent to the 5-gram daily intake of frozen oysters, the degree of induced calcification was insignificant as compared with that following the daily administration of 5 grams of fresh oysters. In experiments in which six rats were fed 5 mg. of cod-liver oil daily, half of them receiving in addition the ash equivalent of 5 grams of fresh oysters daily, there was a difference in the degree of calcification, but the difference was so slight that it was difficult to evaluate. It was not more than that induced by increasing the cod-liver oil 25 per cent.

The poor results obtained in reproduction and rearing of young indicate that oysters contain but little vitamin E. The second generation males were impotent. The females produced some living young but had no capacity to rear them. The character of the diet may be questioned. However, results obtained with clams<sup>20</sup> prepared in the same way as the oysters, and similarly incorporated in the same diet are strikingly different. This strongly indicates that the poor results obtained with oysters with reference to reproduction and rearing of young are to be attributed to a specific deficiency in the oysters rather than to some other factor connected with the diet.

<sup>20</sup> Unpublished data which will appear later.

## Manganese in Steel and Pig Iron<sup>1</sup>

### Volumetric Determination by the Vanadate Method

Lawrence E. Stout and G. C. Whitaker

CHEMICAL LABORATORIES OF WASHINGTON UNIVERSITY, ST. LOUIS, MO., AND MIAMI UNIVERSITY, OXFORD, OHIO

THE potassium permanganate method for the determination of the vanadium content of an alloy steel is based upon the quantitative reduction of the vanadium content from the vanadate to the vanadyl condition and then its reoxidation by means of standard potassium permanganate.<sup>2</sup> In determining the manganese content of a steel the Bureau of Standards official method<sup>3</sup> recommends the oxidation of the manganese content from manganous nitrate to permanganic acid by means of sodium bismuthate, which is added in excess to the cold dilute nitric acid solution of the steel. This quantity of permanganic acid is then determined by filtering and adding a known quantity of ferrous sulfate, the excess of which is back-titrated with standard potassium permanganate.

The ammonium persulfate method for the determination of the manganese content of a steel provides for its quantitative oxidation to permanganic acid by ammonium per-

The work reported herein presents (1) a method for the preparation of standard vanadyl sulfate solution from ammonium metavanadate; (2) a vanadate method for the determination of the manganese content of steels and pig iron; (3) the effect of silver sulfate concentration on the rate of oxidation of manganese from manganous nitrate to permanganic acid.

sulfate in the presence of silver nitrate. If the quantity of manganese in the sample is small, the permanganic acid is then determined colorimetrically. Larger quantities are determined by titration against standard

sodium arsenite solution.

Since in either case the manganese content of the steel is determined by the permanganic acid it can produce, and since the vanadium content of a steel is measured by the amount of standard potassium permanganate required to change the vanadium from the vanadyl to the vanadate state, it occurred to one of the writers that these two facts might be combined to give a method for the determination of the manganese content of steel and possibly pig iron, provided a standard solution of some reduced vanadium salt were available.

#### Preparation of Solutions

**STANDARD VANADYL SULFATE SOLUTION**—To prepare this solution, 10 grams of ammonium metavanadate were dissolved in 600 cc. of water and 40 cc. of 1:1 sulfuric acid. An excess

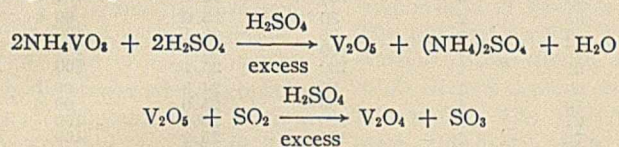
<sup>1</sup> Received September 7, 1927.

<sup>2</sup> Scott, "Metallurgical Analysis," p. 628.

<sup>3</sup> *Ibid.*, p. 331.

of sulfurous acid solution was added and the mixture boiled for 20 minutes to drive off the excess sulfur dioxide. The solution was then cooled, diluted to 2330 cc., and standardized against a sample of steel the manganese content of which had been determined by the bismuthate method. One cubic centimeter of this solution was approximately equivalent to 0.1 per cent of manganese in a 0.200-gram sample.

It is known that vanadium pentoxide is quantitatively reduced to the tetroxide by sulfur dioxide<sup>4</sup> and the reactions are probably as follows:



Vanadyl sulfate solutions were found to be the only ones of all those tried that are suitable for the titration. Vanadyl chloride solutions are unsuited for the purpose. When soluble chlorides are introduced into the solution the permanganic acid tends to interact with the evolution of chlorine. This reaction is not quantitative but was found sufficient to introduce considerable error.

The vanadyl sulfate solutions were prepared from ammonium metavanadate because the salt was more readily available and cost less per gram of vanadium content.

Standard vanadyl sulfate solutions possess a high degree of stability as contrasted with standard sodium arsenite solutions. Six months' standing failed to change the manganese equivalent of the solution. More extended work on this phase of the problem is now in progress.

**STOCK SODIUM CHLORIDE SOLUTION**—4.3578 grams of c. p. sodium chloride were dissolved in water and diluted to 2000 cc.

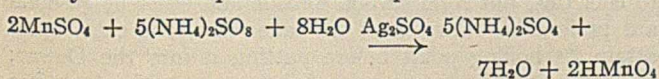
**STOCK SILVER SULFATE SOLUTION**—12.5984 grams of silver nitrate were dissolved in 100 cc. of 10 per cent nitric acid, 40 cc. (1:1) sulfuric acid added, and the solution was boiled down to copious fumes of sulfur trioxide, then cooled and diluted to 2000 cc. These sodium chloride and silver sulfate solutions were made volumetrically equivalent, as the former is used to destroy the activity of the latter before the final titration.

**STOCK AMMONIUM PERSULFATE SOLUTION**—Ten per cent.

#### Method for Steel

Place 0.200 gram of steel in a 250-cc. Erlenmeyer flask and cover with 20 cc. of dilute sulfuric acid (1:3). Heat the flask and contents over a steam plate or low flame for 10 minutes without boiling, then increase the temperature until the liquid boils. When the sample has dissolved, add 5 cc. of stock ammonium persulfate solution and boil until it is decomposed. Cool the reaction mixture, add 10 cc. of stock silver sulfate solution, mix by shaking, then add 10 cc. of the stock ammonium persulfate solution. Allow the mixture to stand 30 minutes, then remove the silver ion by adding 10 cc. of stock sodium chloride solution, and titrate with standard vanadyl sulfate solution.

The chemistry involved is probably as follows: The steel is dissolved in dilute sulfuric acid with the formation of ferrous and manganous sulfates. The former is probably oxidized by the next step to ferric sulfate, thereby being removed from the sphere of action. At the same time the manganous sulfate is quantitatively oxidized to permanganic acid by ammonium persulfate in the presence of silver sulfate:



The excess of ammonium persulfate is rendered inert by removing the silver sulfate with sodium chloride as precipitated silver chloride. At this stage there is no material present to oxidize vanadyl compounds to vanadates except the permanganic acid. The quantity of the permanganic acid present is measured directly by titration with standard vanadyl sulfate solution.

The titrating solution must be added very slowly (drop at a time) as there is little warning of the approach of the end point. An overrun end point may be back-titrated if a standard potassium permanganate solution be available.

#### Special Step for Analysis of Pig Irons

In the analysis of pig irons it is necessary to filter off the undissolved material (graphite) before the silver sulfate is added. From this point the procedure is the same as the one described above.

#### Results

Runs 1 to 20 were made after the method of analysis had been developed. The sample used was Government Standard 9C steel. The numbers on runs 21 to 56 were merely assigned to the samples by the director of the work and have no significance to the reader other than to indicate the number of determinations made upon each sample. Runs 21 to 56 illustrate the results obtained on a group of eleven samples of pig iron and steel, ten of which were commercial samples that had been analyzed by the bismuthate method, while one was a government standard issued by the Bureau of Standards. The analyst knew the correct manganese value of the steel used in runs 1 to 20. However, the manganese values on the samples used in runs 21 to 56 were known only to the director.

The vanadyl sulfate solution was standardized against Bureau of Standards' sample 8C. Twenty titrations required an average of 5 cc. of vanadyl sulfate solution and corresponded to a manganese content of 0.446 per cent. Percentage calculations were then made by direct proportion as follows:

$$\text{Run 1 } 5.0:7.5 = 0.446:x$$

$$x = 0.669 \text{ per cent}$$

Runs 51, 52, and 53 gave poor results because the standard vanadyl sulfate solution was too strong. Better results were obtained when larger samples were used, as in runs 54, 55, and 56. It is possible that a less concentrated vanadyl sulfate solution might give more accurate results, but this point was not investigated because of lack of time.

Table I—Determinations of Manganese in Steel and Pig Iron

NATURE OF SAMPLE <sup>a</sup>	RUN	VANADYL SULFATE Cc.	PER CENT MANGANESE Vanadate method	Correct value
B. S. 9C steel	1	7.5	0.669	0.668 <sup>b</sup>
	2	7.6	0.678	
	3	7.6	0.678	
	4	7.5	0.669	
	5	7.4	0.660	
	6	7.5	0.669	
	7	7.5	0.669	
	8	7.4	0.660	
	9	7.5	0.669	
	10	7.5	0.669	
	11	7.6	0.678	
	12	7.6	0.678	
	13	7.5	0.669	
	14	7.5	0.669	
	15	7.6	0.678	
	16	7.5	0.669	
	17	7.5	0.669	
	18	7.5	0.669	
	19	7.5	0.669	
	20	7.5	0.669	
No. 1B steel	21	9.1	0.82	0.80
	22	9.2	0.83	
	23	9.1	0.82	
No. 2B steel	24	6.7	0.60	0.60
	25	6.7	0.60	
	26	6.7	0.60	
	26	6.7	0.60	

<sup>a</sup> Scott, "Metallurgical Analysis," p. 628.

Table I—Continued

NATURE OF SAMPLE <sup>a</sup>	RUN	VANADYL SULFATE Cc.	PER CENT MANGANESE Vanadate method	CORRECT VALUE
No. 3B pig iron	27	6.6	0.59	0.62
	28	6.6	0.59	
	29	6.7	0.60	
No. 4B steel	30	7.4	0.66	0.65
	31	7.4	0.66	
	32	7.4	0.66	
No. 5B pig iron	33	6.7	0.60	0.62
	34	6.8	0.62	
	35	6.75	0.61	
No. 6B steel	36	7.85	0.70	0.70
	37	8.0	0.71	
	38	7.85	0.70	
No. 7B steel	39	6.5	0.58	0.57
	40	6.45	0.575	
	41	6.4	0.57	
No. 8B steel	42	6.6	0.59	0.60
	43	6.6	0.59	
	44	6.6	0.59	
No. 10B steel	45	6.3	0.56	0.54 <sup>b</sup>
	46	6.1	0.54	
	47	6.2	0.55	
No. 12B steel	48	5.3	0.47	0.462 <sup>b</sup>
	49	5.4	0.48	
	50	5.3	0.47	
No. 12C steel	51	0.71	0.09	0.018
	52	0.67	0.06	
	53	0.7	0.08	
	54	1.12	0.02	
	55	1.12	0.02	
	56	1.1	0.02	

<sup>a</sup> 0.200-gram samples in all but runs 54, 55, and 56, where 1.000-gram samples were used.

<sup>b</sup> These values are given by government analysis; others in this column were obtained by bismuthate method.

In the first fifty-six runs (Table I) ample time and concentration of silver sulfate were desired to permit complete oxidation of the manganese to permanganic acid. It was also desired to know the minimum concentration of silver sulfate and the minimum time of standing that would permit 100 per cent oxidation. By varying the volume of the stock silver sulfate added (and of course using the correct volume of stock sodium chloride), a series of runs (57 to 76, Table II) was made to determine the percentage of manganese oxidized in 30, 60, 120, and 180 minutes. All other conditions within the experiment were the same as before except that larger samples were used to make conditions more extreme.

Table II—Effect of Concentration and Time of Standing on Manganese Oxidation

RUN	(Weight of samples, 0.6000 gram)		Mn OXIDIZED Per cent
	STOCK Ag <sub>2</sub> SO <sub>4</sub> SOLUTION USED Cc.	TIME OF STANDING Minutes	
57	5	30	25.1
	5	60	25.1
	5	120	25.1
	5	180	25.1
	3	30	25.0
61	3	60	25.1
	3	120	25.1
	3	180	25.1
64	3	30	25.0
	2	60	25.1
	2	120	25.1
67	2	180	25.1
	2	30	24.9
70	1	60	25.0
	1	120	25.1
71	1	180	25.1
	1	30	22.2
73	0.5	60	23.6
	0.5	120	24.4
74	0.5	180	24.5
	0.5	30	88.45
75	0.5	60	94.02
	0.5	120	97.2
76	0.5	180	97.6
	0.5	30	97.6

It is noted that 30 minutes' standing is ample when 5 cc. of stock silver sulfate solution is used. Oxidation grows progressively less complete during this period of time when smaller volumes of stock solution have been added. If 1 hour's standing is permitted, the concentration of stock silver sulfate solution added may safely drop to 3 cc., but no lower. If 2 hours' standing is allowed, 1 cc. of the stock silver sulfate solution will answer the need. Even 3 hours' standing failed to effect complete oxidation when only 0.5 cc. of stock solution had been added.

### Conclusions

Standard vanadyl sulfate solutions prepared from ammonium metavanadate may be used to determine volumetrically the manganese content of a steel or pig iron.

This vanadate method eliminates troublesome filtrations or unstable standard solutions required by other methods.

The rate of oxidation of manganous sulfate to permanganic acid by ammonium persulfate in the presence of silver sulfate depends upon the concentration of the silver sulfate present in the solution.

## Laboratory Cooling Device Using Liquid Sulfur Dioxide<sup>1</sup>

A. F. Gill

178 QUEEN ST., OTTAWA, CANADA

IN THE customary "cold test" of castor oil for lubrication of aircraft engines<sup>2</sup> it is necessary to maintain the oil at a temperature of  $-10^{\circ}$  C. for 10 days. An ice-salt mixture is specified as the cooling agent, and to insure a uniform temperature the tube containing the oil is jacketed with a vessel containing a potassium chloride solution with a freezing point of  $-10^{\circ}$  C.

Such an apparatus requires more or less constant attention and frequent renewal of the cooling mixture. Under ordinary conditions the temperature rises considerably overnight. In a search for some means of cooling which would be suitable for a small laboratory lacking mechanical refrigeration, liquid sulfur dioxide was tried. As its boiling point is  $-10^{\circ}$  C., it was proposed to allow the liquid to boil slowly with the tube of oil immersed in it.

This method was quite successful. Slow boiling was maintained by keeping the liquid in a Dewar flask of about 5 cm. internal diameter. The castor oil to be tested was

placed in an 18-mm. test tube as specified and with a thermometer running through the stopper to the bottom of the tube. The stopper was thickly coated with vaseline to exclude moisture and sulfur dioxide. When placed in the sulfur dioxide the oil varied in temperature by less than half a degree, the normal temperature being  $-10.0^{\circ}$  C. The only attention required was the addition of 100 cc. of sulfur dioxide every second day. The actual consumption of sulfur dioxide in 10 days was considerably under 500 cc. There was found to be no inconvenience from sulfur dioxide fumes when the material was kept in a fume cupboard. As the temperature was sufficiently constant no thermometer was needed in routine use and the ends of the test tubes were sealed off in the flame.

Rapid collection of liquid sulfur dioxide from the cylinders was accomplished by using the familiar spiral condenser surrounding a glass reservoir. Ice and salt could be used to cool this, but solid carbon dioxide and ether or gasoline are preferable. Care must be taken that the cold liquid attain its boiling point before putting it into the Dewar; otherwise it will stay supercooled for a considerable time and subject the oil to too low a temperature.

<sup>1</sup> Received January 6, 1928.

<sup>2</sup> British Engineering Standards, Assn. Specification for Aircraft Materials, P. 3.

# An Electrical Solution-Mixing Device<sup>1,2</sup>

K. Hickman and D. Hyndman

EASTMAN KODAK COMPANY, ROCHESTER, N. Y.

**A**FTER the perfection of electrical methods for following analytical titrations,<sup>3</sup> it was inevitable that the chemical engineer should devise similar apparatus for the automatic mixing of solutions. Valves controlled by hydrogen electrodes are now well known,<sup>4</sup> and the patent literature<sup>5</sup> contains references to the pouring together in equivalent proportions almost every kind of liquid.

It is apparent that an electrode placed in a solution for the purpose of exerting control is really an electrical substitute for a chemical indicator. Indicators are broadly of two types, internal and external. Methyl orange used for the ordinary acid-alkali titration is an example of the former; ferricyanide dropped on a white tile for iron estimations is an example of the latter. To the best of our knowledge the indicators used in electrical titrations, either to record or control, have necessarily been of the internal type—the electrode has been placed in the mixing vessel. The present communication describes an electrical titrating or solution-mixing apparatus which works externally and for that reason escapes certain limitations inherent in the ordinary method. It has, of course, other limitations of its own.

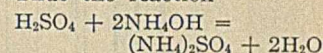
## "Electric Nose"

In popular language, we employ an electrically sensitive "nose" and arrange that a smell is developed or made to cease during the reaction. More explicitly, one of the reactants or else the product of the reaction must contain a volatile or gaseous material which when dissolved in water will render it conducting. It is then possible to blow air or inert gas through the mixing pot, bubble this through water, pass the water into a conductivity cell, and allow the change in conductivity as the water becomes or ceases to become saturated to control the reaction.

The essentials of an apparatus to perform such an operation are few. In Figure 1, pipes *A* and *B*, carrying the solutions, discharge into the mixing vessel, *C*, and thence to their destination via *D*. A stream of air from *E* conveys the indicator gas by way of *F* through the water in *G*, which then trickles into *H*. *H* carries the platinum electrodes, which are in series with a supply of current and a control valve, *K*, or relays and valve *K*, which limits the inflow of the gas-producing solution.

Electrical titration methods in general use employ electrodes immersed in the reacting liquids and give indications of hydrogen or other ion concentrations. The indications have been used by various workers to control automatically the mixing of the two reagents. Such electrical controls may be described as operating internally. The present method uses external gaseous indicators such as sulfur dioxide or ammonia which it detects by an electric "nose" placed over the reacting vessel. The variations in current actuate a valve, which limits the particular solution in excess at that moment. In this connection a special valve mechanism has been devised which requires so little energy for actuation that no amplification or relays are required on the electrical circuit for the nose, even though thousands of gallons of solution be handled each hour. The device is useful both in acidimetry and in oxidation-reduction reactions, particularly with complex mixtures, since only the chosen volatile constituent can effect the control.

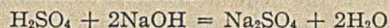
At first it may seem as though there are very few common reactions from which a volatile material may be liberated. This is not so, but if it were it would still be possible to add gas-generating materials as indicators. Thus the reaction



has ammonia available for indicator purposes. If sulfuric acid and ammonia solutions are run into the mixing pot, the acid being independently variable in volume and concentration while the ammonia is controlled by the titrating unit, then ammonia will be checked at the moment a

trace of  $\text{NH}_3$  gas finds its way to the water feeding the conductivity cell.

The more common reaction



evolves no smell, but ammonia may be added in minute quantities to either solution and, being a weak base, will be the last to be neutralized, thus providing the necessary indicator vapor.

An indicator working on the acid side is sulfur dioxide. A trace of sulfite added to the alkaline reagent liberates the gas on becoming acid, and this is exceedingly efficient in activating the conductivity cell.

The method has been found useful in oxidation-reduction reactions. It may be necessary, for instance, to supply exactly equivalent amounts of sulfur dioxide, chlorine, bro-

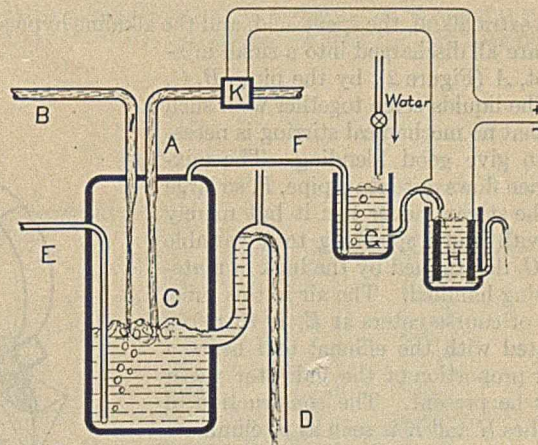


Figure 1—"Electric Nose" for Mixing Solutions

mine, hypochlorite, etc., while keeping the main bulk of the mixture decidedly acid or alkaline, a condition making ordinary titration difficult. If it is desired to destroy hypochlorous acid from waste bleach liquors with the most economical expenditure of thiosulfate, the gas titration method can be employed excellently. The air containing a trace of chlo-

<sup>1</sup> Presented before the Division of Industrial and Engineering Chemistry at the 74th Meeting of the American Chemical Society, Detroit, Mich., September 5 to 10, 1927.

<sup>2</sup> Communication No. 321 from the Research Laboratory of the Eastman Kodak Company.

<sup>3</sup> Clark, "Determination of Hydrogen Ions," Baltimore, 1922; Kolthoff and Furman, "Potentiometric Titrations," New York, 1926.

<sup>4</sup> Crancon, U. S. Patent 1,341,361 (May, 1920).

<sup>5</sup> Edelman, U. S. Patent 1,341,790 (June 1, 1920).

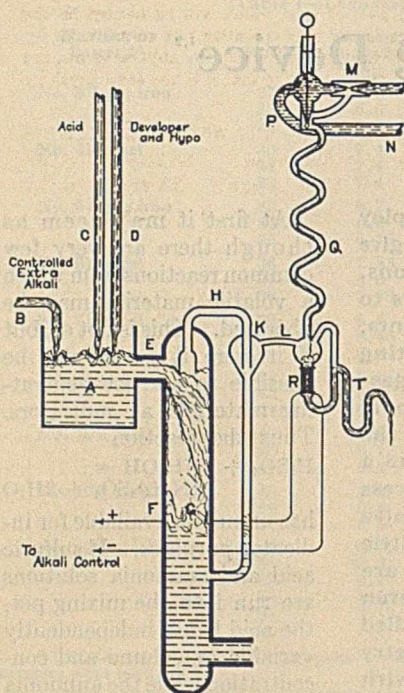


Figure 2—Device for Adding Extra Alkali

to hydrochloric acid and the conductivity of the water rises accordingly.

A reaction which is controlled excellently by the vapor-electric scheme is the neutralization of acid effluents in the presence of thiosulfate. Here sulfur dioxide is the indicating gas. In the complete manufacture of photographic film there are rejected large quantities of sulfuric acid from cotton-nitrating, alkaline developers from film-processing, and thio-sulfate solutions from exhausted fixing baths. If these three liquids are discharged into a common sewer with the acid in excess, not only is sulfur liberated from the thiosulfate, but an odor of sulfur dioxide finds its way into the air. It has therefore been found convenient to augment the mixing by adding just sufficient extra alkali according to the following plan.

#### Addition of Extra Alkali

The extra alkali, the spent acid, and the alkaline hypo solutions are all discharged into a small mixing pot, A (Figure 2), by the pipes B, C, D. The liquids come together with such force that no mechanical stirring is necessary to give good blending. The mixture then flows out into a pipe, F, so large that the stream never fills it but merely falls with much splashing to a variable level, G, determined by the bulk of material being handled. The air in this tube, which of course enters at E, is therefore saturated with the effluent and bears a proper proportion of the indicator vapor if any be present. The construction of the tubes H and K is such as to eliminate splashes from air leaving by L. This comprises the saturator unit. The detector unit consists of a Venturi water pump, M, discharging to waste by N and by-passing a thin stream by way of the needle valve, P, into the spiral column, Q, up which it sucks the vapor-laden air from L. Water passing down Q becomes

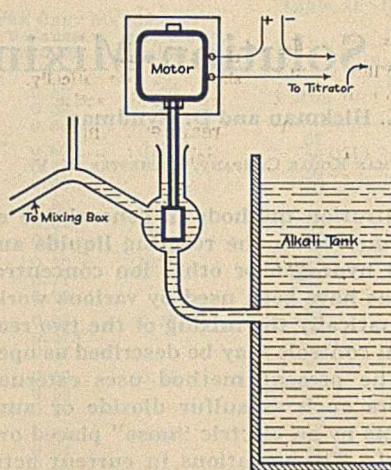


Figure 3—Device for Controlling Flow of Alkali

rine saturates the conductivity cell water. Here the chlorine is oxidized to hypochlorous acid at one pole and at the other reduced

experiments were carried out to devise a simple and robust method of controlling the extra alkali flow with the small current available from the cell. The current might be used (1) directly, (2) to actuate a relay, or (3) after thermionic amplification. The first course has generally been found inadequate, the second is reliable but gives only *on* and *off* control and cannot readily be made to show *how much*. Furthermore, relay apparatus contains iron, and iron rusts in the atmosphere of damp acid-soaked basements. The third alternative was never considered owing to the necessity for skilled maintenance. Recourse was therefore made to the direct utilization of the current in spite of its apparent inadequacy.

With the tap water available the cell had a resistance of about 2000 ohms, falling to one-twentieth of that amount with about 0.1 per cent sulfur dioxide solution in the saturating tube. With such a high resistance it was assumed that there was little danger of serious electrical leakage if the cell were connected directly to the 110-volt house mains. This proved correct, for standing on a damp concrete floor in shoes saturated with dilute acid, no shock was felt on touching the water connection or the wet glass work. There was thus available energy with a zero value of 5 watts, increasing up to a maximum of 100 watts. To obtain sensitivity, however, the apparatus must function when the conductivity merely doubles. The first successful control

saturated with the indicator vapor to approximately the same extent as the original mixing-tank effluent and passes into the cell, R. The capacity of this cell is so small that its contents are changed sufficiently every few seconds. It is made from  $\frac{3}{16}$ -inch Pyrex glass tubing and contains two parallel strips of fine platinum gauze  $\frac{1}{8}$  inch wide and  $1\frac{1}{2}$  inches long with the ends joined to wire and sealed through the glass walls.

*Note*—Pyrex is reputed to give bad seals with platinum. This may be true for delicate physical experiments, but the joint has been found water-tight and durable for the present purpose.

The outflow tubes, T, are arranged so that the water trickling into the cell just comes to the top of the electrodes.

#### Control of Alkali Flow

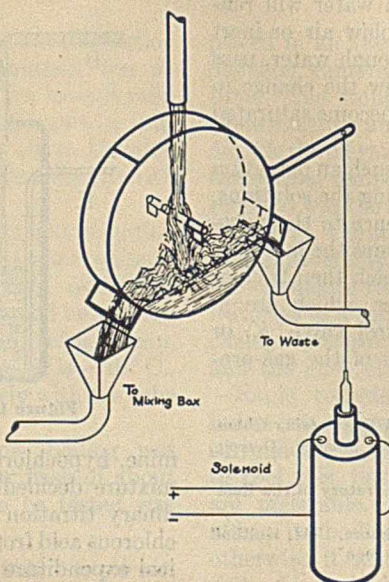


Figure 4—Solenoid Tipping Device

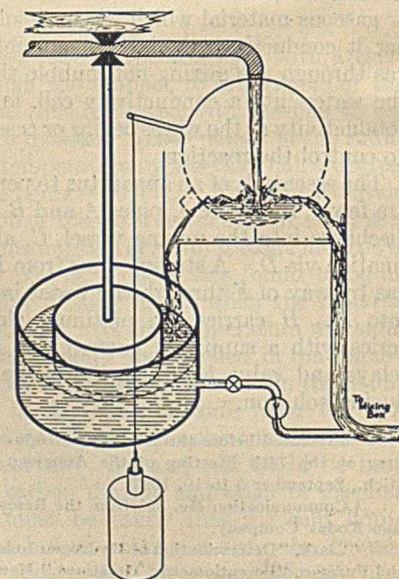


Figure 5—Arrangement for Utilizing Rejected Liquid



was made with the aid of a small  $\frac{1}{16}$ -horsepower Universal motor wired in series with the cell and the 110-volt alternating current supply. The motor was set vertically, with a propeller fastened to its shaft working in a small sump connected with the alkali tank, the level of which was maintained constant. The 5 watts of energy resulting from the zero conductivity just kept the motor turning, any additional current speeding it up and causing alkali to be pumped in varying degrees to the mixing box. The scheme is shown in Figure 3.

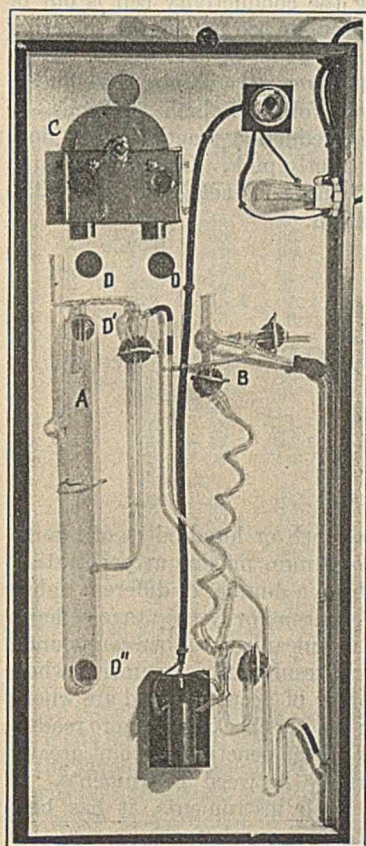


Figure 6—Assembled Unit

Brush trouble and corrosion of the armature windings led to a search for a simpler solution to the problem. A solenoid wound with enough No. 30 cotton-covered copper wire to possess a resistance of about 1000 ohms was built with the idea of actuating a drop valve or conical plug in the alkali-supply pipe. This worked well with direct current, but the detecting cell became fouled with deposits on the electrodes, and bubbles of gas altered the resistance spasmodically. On alternating current, even with the softest of iron cores, very little attractive force was developed.

It was determined, however, to persevere with the solenoid using alternating current and to devise a virtually frictionless valve. This has proved successful

*Note*—Perhaps a twentieth part of that which will be needed in the mixing box. This small portion is the only quantity not controllable by the titrator and represents the minimum below which the apparatus will not shut down automatically. It is easy to arrange that it is less than anything demanded in practice.

stream entering the tipper mostly goes to waste and therefore quickly raises the float valve in the tank. The supply to the tipper is at once limited so that the amount not going to the mixing box is exactly equal to the amount by-passed. Since the control stream and the by-pass stream are both used in neutralization, nothing is wasted. When the demand on the tipped solution fluctuates, the amount sent to the float tank also varies and the stream sent to the tipper becomes adjusted to a new value by the float valve.

An actual unit comprising the saturator, A, detector, B, and tipper, C, mounted in a vertical wooden tray 5 by 2 feet ready for installation but without pipe connections at D, D', and D'', is shown in Figure 6. A celluloid model of the tipper drum is shown separately in Figure 7. The only moving parts—the core of the solenoid and the fulcrum of the tipper—move in oil. The coil box is filled with transformer oil and the knife edges rest in oil troughs. The tipper and box are of monel metal. The saturator tube is 2 inches in diameter and 30 inches long and accommodates 1000 gallons of alkali a day. In building larger units we keep the detector and solenoid the same size, scrap the saturator, and supply the detector with a part of the compressed air used to agitate the mixing pot. There is no difficulty in swinging a very much larger tipper.

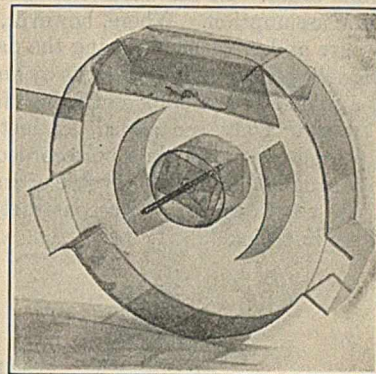


Figure 7—Detail of Tipper

Although a solenoid operating off 60 cycles alternating current exerts only a small pull, it does it in a very interesting manner. First, it is trembling all the time from the current fluctuations, and this removes most of the remaining friction from the tipper bearings. Then again, it becomes increasingly self-choking as the iron enters the core, so that if at any time there is a short circuit in the detector, the iron is sucked in fully and so little current passes that the coil does not get

and apparatus such as will now be described is being used on a works scale in the Eastman Kodak manufacturing plants for different purposes.

Let us suppose that there is an indefinite supply of a certain liquid flowing to waste and that we wish to partition off a variable amount for use. We can allow the whole stream to tumble into a hollow drum (Figure 4) pivoted axially so that it may be rotated in perfect balance through a few degrees. We can allow the stream to escape from the barrel by either or both of two openings having short delivery pipes disposed radially. Because the streams leave radially, they exert no turning moment on the drum, however unequally they issue from the openings. It therefore requires no effort to tip the drum (other than that absorbed by bearing friction) no matter in what proportion the stream happens to be divided. If a lever on the drum is connected with the core of a solenoid actuated by the vapor detector, solution will be deflected to or from the mixing box whenever the water in the cell changes conductivity.

Let us suppose further that it is not economical to let the rejected stream in Figure 4 run to waste. We can obviate it very simply as follows: The rejected portion is allowed to fall into a small shallow tank (Figure 5), in which rests a float actuating a valve controlling the influx into the tipping drum. From the float tank a very small stream is by-passed to the mixing box. When the partitioning apparatus is started the large

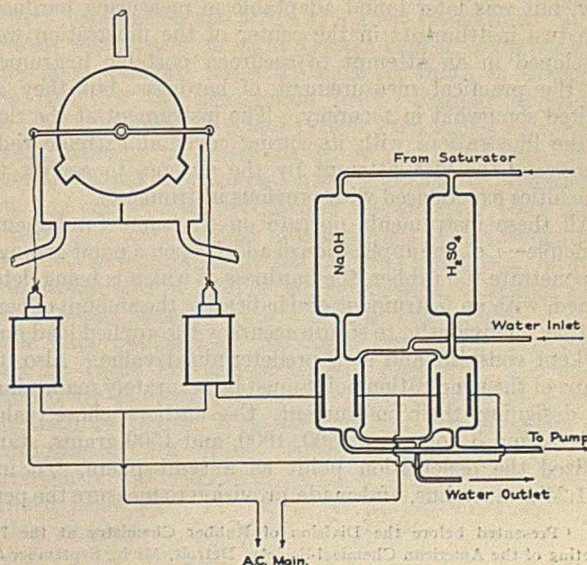


Figure 8—Application of Titration

perceptibly warmer than when working normally. Nevertheless, we run the cell in series with a 60-watt lamp as a protection on the lead which does not pass through the coil.

The weight of the iron core and the zero pull of the solenoid are balanced by a counter weight on the tipper. Moreover, we have assumed that the conductivity of the water feeding the Venturi pump and thence the cell is of a constant and negligible order. In the Great Lakes region of America this is a safe assumption. Where, however, the water supply is not so pure and is variable during the day, it is necessary to replace the counterbalance weight by another iron core actuated by a solenoid and compensating cell fed with a second stream of water. Only the added conductivity conferred by the indicator vapor will then be recorded.

This double scheme is capable of an interesting application. Dilute solutions of two gaseous materials such as ammonia and sulfur dioxide may be mixed, a saturator and detector

being coupled with each cell. In series with one is an absorption tower carrying alkali, in the other a wash bottle holding sulfuric acid. The one chain allows ammonia only to pass, the other, sulfur dioxide. Thus, perfect balance of the tipper is secured during variation of the load (Figure 8).

We are using the scheme successfully for other reactions and have considered it advisable to seek patent protection.

It is not possible to give definite figures with regard to performance. If the mixing pot is too small or too large, or the water stream feeding the conductivity cell is out of adjustment, the tipper will oscillate too far in each direction and cause alternate over- and under-neutralization. With correct adjustment, which is very easy to obtain, the effluent, colored with phenolphthalein for acid-alkali reactions, or permanganate with oxidation-reduction reactions, will fluctuate between colorless and faintly pink. Caught in a large tank, the effluent of several hours is as nearly neutral as the product of a laboratory titration.

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## A Hardness Tester for Rubber<sup>1</sup>

Erle C. Zimmerman and R. W. Brown

THE FIRESTONE TIRE AND RUBBER COMPANY, AKRON, OHIO

VARIOUS forms of instruments have long been in use for measuring the hardness of vulcanized rubber. This use has undoubtedly been more or less extensive, but hardness has been rarely mentioned in the literature on rubber. Some of the earlier instruments were not direct-indicating, could not be operated by hand, and required the preparation of special samples. The first hand-operated instruments were a step in simplification, but were objectionable because of a low degree of accuracy and sensitivity. In attempting to overcome the objectionable features of these instruments, an instrument of improved design was developed which has been in use for several years and found to answer all the requirements satisfactorily.

### Development of Penetrometer

Several instruments constructed to measure the hardness of vulcanized rubber are shown in Figure 1. The one at the extreme left was originally developed for measuring plastic flow, but was later found adaptable in measuring hardness. The two instruments in the center of the illustration were developed in an attempt to secure a portable instrument for the practical measurement of hardness, but they are limited somewhat in accuracy. The instrument at the right of the illustration, with its spring cover at extreme right, represents the first attempt by the authors to correct the difficulties experienced with previous instruments.

All these instruments operate on the same fundamental principle—i. e., the application of a load upon a point arranged to penetrate the rubber, the hardness of which is being determined, with an instrument dial indicating the amount of penetration. Obviously, to secure accuracy the applied load must be kept constant and at a predetermined value. Also, the shape of the penetration point must be accurately maintained. In designing their instrument, the authors chose values of 1, 2, and 3 pounds, or 500, 1000, and 1500 grams, standardized the penetration point as a semi-sphere,  $\frac{3}{64}$  inch or 1.25 mm. radius, and made provision to measure the pene-

tration in thousandths of an inch or hundredths of a millimeter with 0.100 inch or 2.50 mm. maximum penetration. These values were selected from a number of different values tried out and found to cover satisfactorily the range of hardness ordinarily encountered in vulcanized rubber compounds.

Developments to date have resulted in instruments whose readings repeat to a high order of accuracy, and are wholly interchangeable. Means for readily checking the zero reading and for determining the load on the penetration point greatly assisted in securing uniformity between instruments. In the actual construction of such instruments, it has been found necessary to make the spring relatively long so that the change in load between minimum and maximum penetration is negligibly small. This feature constitutes one of the very serious faults with the early instruments. The improvement made in this respect is shown in the instrument at the right in Figure 1. The design must be such as to render the instrument readily portable and adaptable for rapid hardness determinations of various shaped pieces of rubber.

In order to illustrate the effect of design on the accuracy of hand hardness testers, six representative rubber compounds were tested with the penetrometer, durometer, and densimeter. The results are shown in Table I, and need no discussion.

The instrument shown in Figure 2 is an adaptation of the original hand instrument mounted on a support. Incidentally, this mounted instrument eliminates two sources of inaccuracy which occur in the use of hand instruments: (1) the rubber is pressed against the foot of the instrument with a definite and predetermined pressure, and (2) the instrument is positively aligned with the face of the rubber. These two conditions can be satisfactorily met by a skilled operator using the hand instrument.

The desirability of applying the instrument to the rubber with a definite force resulted in the design and construction of the improved model, the mounted form of which is shown in Figure 3. By removing the instrument from its supporting bracket, it can be conveniently used as a hand instrument. Arrangements are provided whereby it is impossible to apply

<sup>1</sup> Presented before the Division of Rubber Chemistry at the 74th Meeting of the American Chemical Society, Detroit, Mich., September 5 to 10, 1927.

the instrument to the rubber with a force greater than the predetermined value. The cross-sectional view in Figure 4 shows how this has been accomplished. The outer shell, 1, fits in the supporting bracket and is moved up and down by a rack and pinion. The casing, 2, with its ends, 4 and 6, acts as a plunger inside of the shell, 1, and is held under uniform tension by spring 3. The collar, 9, is firmly attached to the shell, 1, and serves as a support for spring 3. The spring 7 with its support, 8, and the point 5 are standardized parts used in all types of penetrometers. This mechanism is attached to the indicating dial shown at upper part of end 6.

Table I—Comparative Results with Various Hardness Testers

PENETROMETER				PENETROMETER			
In 0.001 inch	In 0.01 mm.	DUROM-ETER	DENSIM-ETER	In 0.001 inch	In 0.01 mm.	DUROM-ETER	DENSIM-ETER
STOCK 1				STOCK 4			
90	225	44	90	59	147	57	49
92	230	45	95	58	145	55	46
91	227	47	89	58	145	56	48
89	223	45	93	57	143	58	52
92	230	46	95	59	147	56	43
Av. 90.8	227	45.4	92.2	58.2	145.4	56.8	47.6
Var. 3	7	3	6	2	4	3	9
STOCK 2				STOCK 5			
83	207	47	78	37	92	66	28
84	210	48	79	38	94	67	25
83	208	46	83	38	94	66	29
84	210	47	81	37	92	68	28
84	210	48	81	36	90	65	33
Av. 83.6	209	47.2	80.2	37.2	92.4	66.4	28.6
Var. 1	3	2	5	2	4	3	8
STOCK 3				STOCK 6			
78	195	52	65	15	38	82	12
79	197	50	70	16	40	86	17
80	200	49	73	17	43	83	15
78	195	50	69	15	38	83	9
79	198	50	71	16	40	84	11
Av. 78.8	197	50.2	69.2	15.8	39.8	83.6	12.8
Var. 2	5	3	8	2	5	4	8
AVERAGE VARIATION IN STOCKS 1 TO 6				RANGE FROM STOCK 1 TO STOCK 6			
2	4.7	3	7	75.0	187.8	38.2	79.4

The penetration secured on stocks of varied hardness with the loads of 1, 2, and 3 pounds or 500, 1000, and 1500 grams on the penetration point are shown in Table II and Figure 5. It will be noted that the 3-pound (1500-gram) spring covers the range of hardness of various rubber compounds quite adequately. If the interest is confined to soft-rubber com-

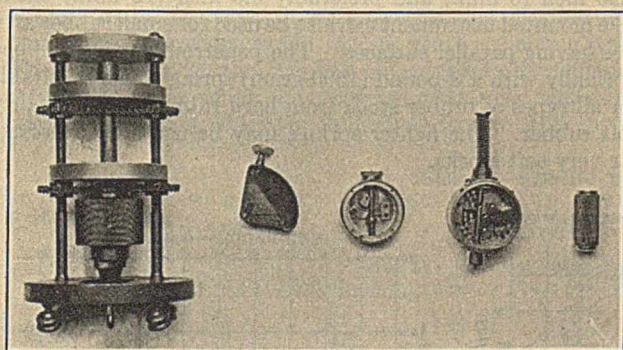


Figure 1—Various Forms of Hardness Testers

pounds, the 1-pound (500-gram) spring is recommended. The 2-pound (1000-gram) spring is only necessary for some types of highly specialized testing.

The maximum penetration permissible for accurate hardness indication occurs at the point beyond which the stock takes a detectable permanent set. For the majority of rubber compounds a penetration of around 0.050 inch (1.25 mm.) has been found desirable and the permissible maximum in nearly all cases lies at or slightly above 0.100 inch (2.50 mm.). Hence the load on the penetration point should be adapted to the hardness of the rubber compound so that the penetration lies within the above limits.

Table II—Penetration with Different Spring Values

TYPE OF STOCK	PENETRATION IN 0.001 INCH			PENETRATION IN 0.01 MM.		
	WEIGHT OF SPRING					
	3 lbs.	2 lbs.	1 lb.	1500 grams	1000 grams	500 grams
Very soft	No reading	99	55	...	248	137
Soft	81	64	36	202	160	90
Medium	65	50	28	162	125	70
Hard	44	31	18	110	77	45
Very hard	13	9	4	32	22	10

The thickness of the stock also influences the instrument reading. The extent of this influence is shown in Table III. From this it is evident that test slabs should be at least 0.5 inch (12 mm.) thick and in all comparisons slabs of the same thickness should be used. Hardness on test slabs as thin as 0.25 inch (6 mm.) can of course be compared with each other, but it is well to test a 0.5-inch (12-mm.) slab of one of the stocks under consideration for reference. It is desirable to support all stocks less than 1 inch (25 mm.) thick on a flat, rigid surface whenever possible. However, reasonably accurate results can be secured by a skilled operator with a hand instrument on such irregular surfaces as the non-skid button of the pneumatic tire.

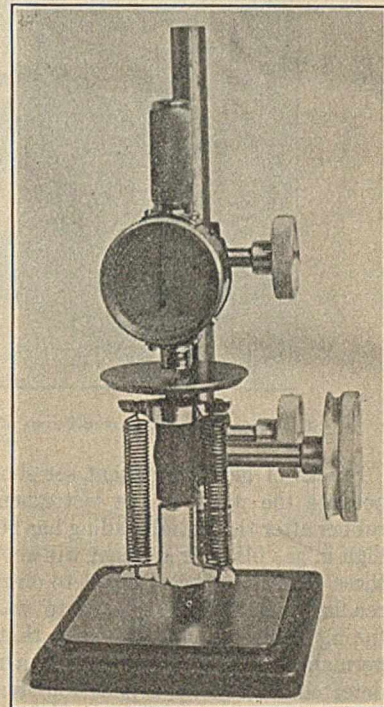


Figure 2—Mounted Penetrometer

#### Comparison of Penetration with Stress at a Given Elongation

It was considered advisable to determine the relationship between penetration and stress at a given elongation. Comparisons were made on eight typical rubber compounds of fairly good quality. Slabs 0.5 inch (12 mm.) in thickness were used for the penetration tests. Regular dumb-bell test pieces 0.10 inch (2.5 mm.) thick were tested on a Scott testing machine to determine stress and elongation data. Stress at 200 per cent elongation was chosen after preliminary tests had shown that satisfactory comparative tests could be made over the full range of compounds at this elongation. It is possible that stress at 100 per cent elongation, or even lower would give a still better comparison, although such measurements cannot be made in most laboratories.

The data obtained on the eight compounds have been listed in Table IV, and plotted in Figure 6. The curve obtained by plotting penetration against stress at a fixed elongation was found to be quite regular, but of course the relationship is not linear. Similar curves may be used conveniently for reference to show approximate relation between penetration and stress as measured on the Scott testing machine. The eight compounds compared were typical for the different types of use and were given what was considered the best commercial cure.

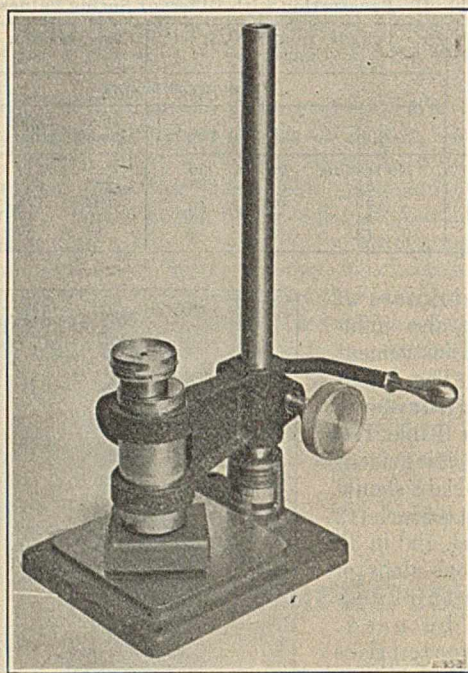


Figure 3—Improved Form of Penetrometer

Stocks of high permanent set show abnormal penetration because the point of the instrument slowly penetrates the rubber after the initial reading has been taken. Many stocks high in gas black or softener will show this behavior. Under these conditions it is difficult to obtain a definite penetration reading, and it is necessary to wait a few seconds before taking the reading. The fact that the effect of excessive permanent set or "logginess" in a rubber compound can be detected readily on a penetrometer makes this instrument of still further value to the rubber technologist.

#### Use of Penetrometer in Testing Vulcanized Rubber

The portable and mounted penetrometers are both useful instruments for the rubber technologist. The hand instrument is particularly useful in measuring hardness of pneumatic-tire treads. With rare exceptions, tire sections are so

Table III—Effect of Test Slab Thickness on Penetration

TYPE OF STOCK	THICKNESS OF TEST PIECE	PENETRATION IN 0.001 INCH	THICKNESS OF TEST PIECE	PENETRATION IN 0.01 MM.
	Inches		Mm.	
Soft	0.125	58	3.18	145
	0.250	71	6.35	177
	0.375	77	9.53	192
	0.750	81	19.05	202
Medium	0.125	50	3.18	125
	0.250	58	6.35	145
	0.375	63	9.53	157
	0.750	65	19.05	162
Hard	0.125	39	3.18	97
	0.250	42	6.35	105
	0.375	43	9.53	107
	0.750	44	19.05	110

Table IV—Penetration and Stress Data

TYPE OF STOCK	STRESS		PENE-TRATION IN 0.001 INCH	STRESS		PENE-TRATION IN 0.01 MM.
	200% elong.	Break		200% elong.	Break	
	Lbs./sq. in.			Kg./sq. cm.		
Inner tube	140	2800	98	9.84	197	245
Zinc oxide stock	275	3125	81	19.3	219.5	202
Zinc oxide stock	340	3300	73	23.9	232	182
Zinc oxide stock	415	3550	66	30.3	249.5	165
Solid tire	655	2800	41	46.0	197	102
Pneumatic tire tread	750	3800	35	52.7	267	87
Pneumatic tire tread	1050	3200	27	73.8	225	67
Pneumatic tire tread	1800	3300	19	126.5	232	47

thick that the effect of thickness on the penetration value is negligible. The hand instrument may also be used conveniently for solid tires and miscellaneous molded articles such as shock insulators, motor supports, heels, soling, etc. In no case is it necessary to cut rubber products and prepare special samples for penetration tests. The penetrometer can be operated with great speed, it being possible to make as many as fifteen tests per minute so that a large volume of product can be tested in a short time. The mounted instrument is, of course, more accurate than the portable instrument, and it serves well for laboratory control work or research compounding. A multiple-cavity mold can be used to advantage in making slabs of uniform thickness. As pointed out previously, these slabs should be at least 0.25 inch (6 mm.) and preferably 0.5 inch (12 mm.) thick. The mounted instrument can also be used for small rubber articles having parallel surfaces. The penetrometer is equipped normally with a 3-pound (1500-gram) spring which is suitable for all types of rubber stock from hard rubber down to fairly soft rubber. The lighter springs may be used to advantage for very soft stocks.

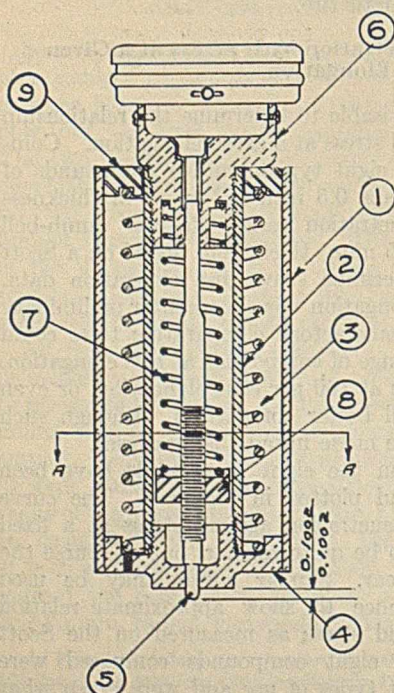


Figure 4—Cross Section of Penetrometer

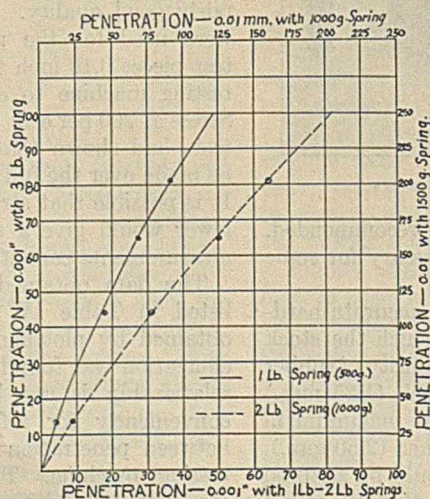


Figure 5—Penetration with Different Spring Values

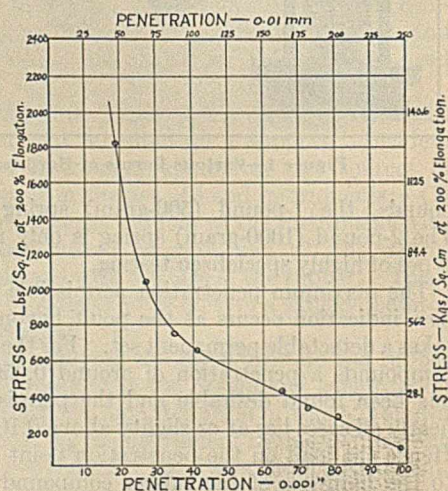


Figure 6—Penetration and Stress

# The Optimum Soil Reaction of the Sugar Beet<sup>1</sup>

O. Arrhenius

PASOEROEAN, JAVA

**D**URING recent years the writer has been conducting a series of large-scale investigations concerning the growth and yield of the sugar beet in connection with the soil reaction.<sup>2</sup> These investigations have been of great service to the industry. They may be considered as a first step towards the control of agricultural products, just as in every well-managed factory the production is strictly controlled.

## Experimental Work

Through a series of pot experiments (Table I) it was found that the beet grows best on a neutral or slightly alkaline soil (pH 7.0 to 7.5). This opinion was sustained by the results of an investigation of about twenty farms in southern Halland, a province in southern Sweden (Table II), where the reaction of the fields was compared with the yield of beets.

Table I—Pot Experiments with Sugar Beet in Different Acid Soils

1923:										
pH	3.9	4.7	6.0	6.6	7.5	7.9	8.6	8.8	9.2	
Relative yield	0	71	93	93	99	71	90	100	1	
1924:										
pH	4.2	5.0	6.2	6.5	7.1	7.8	8.3			
Relative yield	27	57	68	71	81	73	100			

Table II—Relative Yield of Sugar Beets on About Twenty Farms in Southern Halland

Relative yield	34	59	82	92	100
pH	Less than 6.0	6.0 to 6.3	6.4 to 6.6	6.7 to 6.9	Above 7.0

It was then decided to carry out the investigation on a semicommercial scale for one year. Director Cederborg of Staffanstorps, a sugar factory in southern Sweden, made such an investigation covering the soil reaction of the whole factory district in 1923. (Table III)

The same year a similar examination was made on a large number of farms in southern Halland.

The results of these investigations indicated that their practical application would be of great economic value. Therefore in 1924 the Swedish Sugar Factories Company investigated the whole area planted that year with sugar beet and also that which should be beet land in 1925.

Table III—Relative Yield in the Staffanstorps District

pH	6.0 to 6.1	6.2 to 6.3	6.4 to 6.5	6.6 to 6.7	6.8 to 6.9	7.0 to 7.1	7.2 to 7.3	7.4 to 7.5	7.6 to 7.7
Relative yield	67	78	87	88	88	96	99	100	89

Table IV—Relative Sugar-Beet Yield in Whole South Sweden Area

pH	6.0 to 6.1	6.2 to 6.3	6.4 to 6.5	6.6 to 6.7	6.8 to 6.9	7.0 to 7.1	7.2 to 7.3	7.4 to 7.5	7.6 to 7.7	7.8 to 7.9
Relative yield:										
1924	78	81	86	90	93	96	97	99	97	93
1925	80	89	90	93	96	97	99	99	97	96

A large amount of material was gathered regarding the factors influencing the sugar-beet culture, but only the results of the investigations regarding the soil reaction will be mentioned in this paper. The results (about 40,000 soils analyzed every year) are compared with the yield from every farm (about 15,000) and then the average for each factory district is calculated. The yield for each soil is reported as per cent of this highest average, and from all these factory averages the general average is then deduced. These averages for 1924 and 1925 are found in Table IV.

From the illustration it is seen that results from the different investigations agree very well.

Note—As the field investigations only reach to pH 8, and therefore no comparison can be made between the yields on more alkaline soils, the graphs give only the results at pH 8 and lower.

We can therefore conclude that, for sugar beets at least, the results of the pot experiments are identical with those of the field investigations. A few years ago Wherry<sup>3</sup> pointed out that the results obtained by pot experiments as carried out by the writer could not be used as a standard for the field treatment, and the investigation described herein was undertaken to check previous data which formed the basis of his conclusion.

As we have seen, the sugar beet gives the best yield at a pH between 7.0 and 7.5. Many of the soils of the beet districts in southern Sweden are acid (Table V). A liming would therefore be of great benefit.

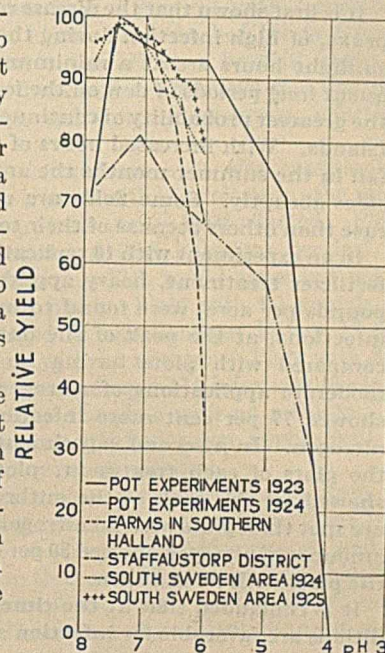


Table V—Acidity of Sugar Beet Soils in Southern Sweden

pH	5.5 to 5.9	6.0 to 6.4	6.5 to 6.9	7.0 to 7.4	7.5 to 7.9	8 to 9
% of area	1	11	29	43	15	1

From the curves and the results of the soil acidity investigations one may deduce the probable increases in the yield for the different districts if a liming was thoroughly carried out. In some districts liming will be of very little benefit, in others it will give excellent results.

Because of the good results obtained by the soil acidity investigations, they are being continued for seven years (about one crop rotation). Each year the soils which the following year will be planted with beets are examined with regard to the soil reaction and advices are distributed to the farmers regarding the soil treatment. But the investigations are not limited to this. In districts where large areas are of acid reaction the whole district or the more important farms are examined, thus enabling the farmer to choose those soils and those fields which are best fit for the sugar-beet culture, leaving the rest for plants which thrive better on that reaction.

<sup>1</sup> Received May 31, 1927.

<sup>2</sup> "Bodenreaktion und Pflanzenwachstum," Akad. Verlagsges., Leipzig, 1926.

<sup>3</sup> *Ind. Eng. Chem.*, 16, 826 (1924).

# Effect of Fertilizer Constituents on the Eye-Spot Disease of Sugar Cane<sup>1</sup>

H. Atherton Lee and J. P. Martin

EXPERIMENT STATION, HAWAIIAN SUGAR PLANTERS' ASSOCIATION, HONOLULU, T. H.

A method of measuring quantitatively the degree of infection of a fungous disease of sugar cane called "eye spot" is described. The effect of the usual constituents of commercial fertilizers upon this disease has been determined by this method.

It is first shown that the disease reaches a peak, or several peaks, of high infection during the winter months, when sunlight hours are at a minimum and there are consequent long periods of dew on the leaves, and when there is the greatest probability of continued rains in the Hawaiian Islands. With increased hours of sunlight and less rainfall in the summer months the amount of infection subsides abruptly. Some fields are more subject to the disease than others because of their topography.

In an experiment with 10 replications of the plots of each fertilizer treatment, heavy applications of nitrogen (300 pounds per acre) were found to increase the numbers of infections, at the peak of the outbreak, 238 per cent as compared with plots having no nitrogen. Plots with moderate applications of nitrogen (65 pounds per acre) showed 77 per cent more infections than plots with no nitrogen. In a second experiment with 6 replications of the plots of each treatment, plots with high nitrogen showed, at the peak of the outbreak, 273 per cent more eye spot than plots with no nitrogen. Plots with moderate amounts of nitrogen showed 80 per cent more eye spot than the plots with no nitrogen.

It is concluded that at the time of the year when conditions are favorable for infection applications of nitrogen

fertilizers should be avoided in fields subject to this disease. The optimum time for the application of nitrogen fertilizers is in the months of April, May, June, and July, in the Hawaiian Islands.

It is of significance that in the first experiment although nitrogen fertilizers did not give the growth response to the cane which phosphoric acid did, the cane showed a much greater reaction to eye spot in the nitrogen plots. In the second experiment nitrogen fertilizers gave no growth response to the cane, yet the nitrogen-treated plots showed much the greatest eye-spot reaction. Apparently, therefore, eye-spot infection is correlated, not with more vigorous growth, but with some physiological reaction of the cane produced by the nitrogen.

In the first two experiments, at the peaks of infection, plots with no phosphoric acid showed more eye spot than plots with high phosphoric acid (400 pounds per acre). The experimental differences were not great enough to be considered significant, but at least it can be concluded that growth response in cane from phosphoric acid does not result in increased eye spot.

In three separate experiments with adequate replications of the plots of each treatment, plots with no potash showed more infection at the peaks of the disease than plots with high applications of potash. The differences in the degree of infection were not great enough to be entirely significant but, being obtained so consistently, are highly suggestive that potash fertilizer applications result in slightly lessened infection.

THE disease of sugar cane with which the writers have been dealing is called "eye spot," and is caused by the fungus *Helminthosporium sacchari* Butler. This disease is a minor leaf spot on most varieties of sugar cane, causing losses which are considered negligible, but some varieties are severely affected. The most commonly planted and most productive variety of sugar cane in the Hawaiian Islands at present is a hybrid, Hawaii 109, which has the one serious defect of being highly susceptible to eye spot. *Helminthosporium* infections on this variety under the proper weather conditions become so numerous as to result ultimately in a top rot of the cane stalk, and sometimes very serious losses occur.

The disease is one of seasonal occurrence. The spores of the causal fungus require moisture for germination and infection of the cane leaf. In the months of shortened length of sunlight—October to March—when there is dew on the leaves for long periods, and also coincidentally a greater probability of rainfall, the infection rapidly increases. Some fields because of their topography when sloping to the north away from the sun or shaded by high cliffs—are more commonly affected than others. Low-lying fields near bogs or large surfaces of water, which act as large sources for the evaporation of water and so indirectly for atmospheric humidity and dew formation, are also commonly affected.

There have been divergent opinions among planters in the Hawaiian Islands regarding the effect of the various fer-

tilizer constituents on the severity of eye spot. Some planters maintained that nitrogen fertilizers applied prior to the period favorable for infection would stimulate rapid growth and that the same amount of infection would result in more severe injury to slow-growing cane than to fast-growing cane. Other planters were of the opinion that nitrogen fertilizers made the cane plant more susceptible to the disease. The opinion was also strongly advanced that potash fertilizers would control the disease.

To establish the relation of these fertilizer constituents to the susceptibility of the cane plant to infection by the eye-spot fungus, the following experiments were conducted.

## Methods of Measuring Degree of Infection

To test the effects of fertilizer constituents on *Helminthosporium*, a field of a susceptible variety of sugar cane was selected in an area where the topography and weather conditions indicated the probable occurrence of eye spot. Plots were laid out in the field, usually with ten rows of cane to a plot, each row 30 feet long; the area of each plot was therefore about  $\frac{1}{28}$  acre. In each experiment enough plots were laid out to have at least six, and if possible eight or ten, replications of each fertilizer treatment. The fertilizers were then applied during August, the time of the year just previous to the usual period for infection. In Experiment I, for example, the scheme of fertilizer applications was as follows:

Plots W. Phosphoric acid and potash fertilizers in usual amounts but no nitrogen.

<sup>1</sup> Received September 14, 1927.



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In an experiment with 10 replications of the plots of each fertilizer treatment, heavy applications of nitrogen (300 pounds per acre) were found to increase the numbers of infections, at the peak of the outbreak, 238 per cent as compared with plots having no nitrogen. Plots with moderate applications of nitrogen (65 pounds per acre) showed 77 per cent more infections than plots with no nitrogen. In a second experiment with 6 replications of the plots of each treatment, plots with high nitrogen showed, at the peak of the outbreak, 273 per cent more eye spot than plots with no nitrogen. Plots with moderate amounts of nitrogen showed 80 per cent more eye spot than the plots with no nitrogen.

It is concluded that at the time of the year when conditions are favorable for infection applications of nitrogen

fertilizers should be avoided in fields subject to this disease. The optimum time for the application of nitrogen fertilizers is in the months of April, May, June, and July, in the Hawaiian Islands.

It is of significance that in the first experiment although nitrogen fertilizers did not give the growth response to the cane which phosphoric acid did, the cane showed a much greater reaction to eye spot in the nitrogen plots. In the second experiment nitrogen fertilizers gave no growth response to the cane, yet the nitrogen-treated plots showed much the greatest eye-spot reaction. Apparently, therefore, eye-spot infection is correlated, not with more vigorous growth, but with some physiological reaction of the cane produced by the nitrogen.

In the first two experiments, at the peaks of infection, plots with no phosphoric acid showed more eye spot than plots with high phosphoric acid (400 pounds per acre). The experimental differences were not great enough to be considered significant, but at least it can be concluded that growth response in cane from phosphoric acid does not result in increased eye spot.

In three separate experiments with adequate replications of the plots of each treatment, plots with no potash showed more infection at the peaks of the disease than plots with high applications of potash. The differences in the degree of infection were not great enough to be entirely significant but, being obtained so consistently, are highly suggestive that potash fertilizer applications result in slightly lessened infection.

THE disease of sugar cane with which the writers have been dealing is called "eye spot," and is caused by the fungus *Helminthosporium sacchari* Butler. This disease is a minor leaf spot on most varieties of sugar cane, causing losses which are considered negligible, but some varieties are severely affected. The most commonly planted and most productive variety of sugar cane in the Hawaiian Islands at present is a hybrid, Hawaii 109, which has the one serious defect of being highly susceptible to eye spot. *Helminthosporium* infections on this variety under the proper weather conditions become so numerous as to result ultimately in a top rot of the cane stalk, and sometimes very serious losses occur.

The disease is one of seasonal occurrence. The spores of the causal fungus require moisture for germination and infection of the cane leaf. In the months of shortened length of sunlight—October to March—when there is dew on the leaves for long periods, and also coincidentally a greater probability of rainfall, the infection rapidly increases. Some fields because of their topography when sloping to the north away from the sun or shaded by high cliffs—are more commonly affected than others. Low-lying fields near bogs or large surfaces of water, which act as large sources for the evaporation of water and so indirectly for atmospheric humidity and dew formation, are also commonly affected.

There have been divergent opinions among planters in the Hawaiian Islands regarding the effect of the various fer-

tilizer constituents on the severity of eye spot. Some planters maintained that nitrogen fertilizers applied prior to the period favorable for infection would stimulate rapid growth and that the same amount of infection would result in more severe injury to slow-growing cane than to fast-growing cane. Other planters were of the opinion that nitrogen fertilizers made the cane plant more susceptible to the disease. The opinion was also strongly advanced that potash fertilizers would control the disease.

To establish the relation of these fertilizer constituents to the susceptibility of the cane plant to infection by the eye-spot fungus, the following experiments were conducted.

## Methods of Measuring Degree of Infection

To test the effects of fertilizer constituents on *Helminthosporium*, a field of a susceptible variety of sugar cane was selected in an area where the topography and weather conditions indicated the probable occurrence of eye spot. Plots were laid out in the field, usually with ten rows of cane to a plot, each row 30 feet long; the area of each plot was therefore about  $\frac{1}{28}$  acre. In each experiment enough plots were laid out to have at least six, and if possible eight or ten, replications of each fertilizer treatment. The fertilizers were then applied during August, the time of the year just previous to the usual period for infection. In Experiment I, for example, the scheme of fertilizer applications was as follows:

*Plots W.* Phosphoric acid and potash fertilizers in usual amounts but no nitrogen.

<sup>1</sup> Received September 14, 1927.



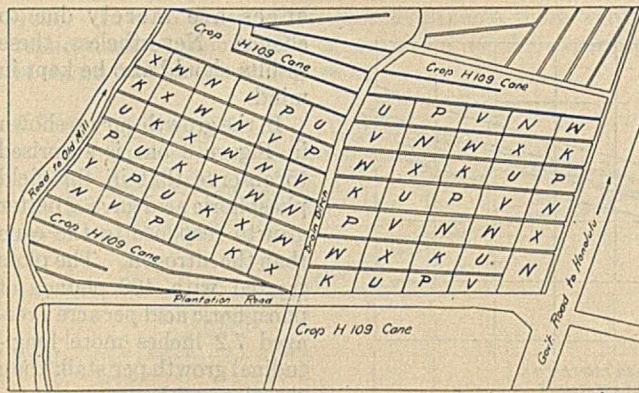


Figure 1—Arrangement of Plots as in Experiment I

- Plots I. Usual amounts of phosphoric acid and potash but a higher amount of nitrogen.
- Plots V. Usual amounts of nitrogen and potash but no phosphoric acid.
- Plots P. Usual amounts of nitrogen and potash and a high application of phosphoric acid.
- Plots U. Usual applications of nitrogen and phosphoric acid but no potash.
- Plots K. Usual amounts of nitrogen and phosphoric acid and high amounts of potash.
- Plots X. Applications of nitrogen, phosphoric acid, and potash, all in usual amounts.

A chart showing the arrangement of the treatments in Experiment I is shown in Figure 1, and gives an idea of the arrangement of the other experiments as well.

Shortly after the fertilizers were applied and before eye-spot infection had begun to become numerous, 20 stalks were selected in each plot and a strip of red cloth was tied to each stalk for future identification. On each such marked stalk the third leaf from the youngest visible or most recently opened flat leaf was selected and the number of infections counted. In Experiment I, there being 20 stalks to a plot, and 1 leaf to each stalk, there were thus infections counted on 20 leaves per plot. There being 10 plots of each series of fertilizer treatment, there were thus 200 leaves per treatment upon which infections were counted. The numbers of infections on these 200 leaves were then totaled and the average number of infections per leaf for each type of fertilizer treatment calculated. The counts of infections were recorded at 2-week intervals, always on the same marked stalks but usually on new leaves, since in a period of 2 weeks at least one new leaf would have opened on each stalk, making the third from the youngest flat leaf a new leaf to be counted in each case.

**Methods of Making Cane-Growth Measurements**

At the same time that eye-spot counts were made, growth measurements were made, briefly as follows: Ten of the 20 marked stalks in each plot were selected and a small wooden peg was driven into the ground to form a standard point or bench mark from which to measure the stalk growth. The measurement was made from this bench mark to the highest visible juncture of leaf blade and

leaf sheath. With 10 stalks thus measured per plot and 10 replications of the plots of each fertilizer treatment, there were therefore 100 stalk measurements to be averaged to obtain the average longitudinal growth per stalk per treatment.<sup>2</sup> These growth measurements were obtained at 2-week intervals.

**Experiment I**

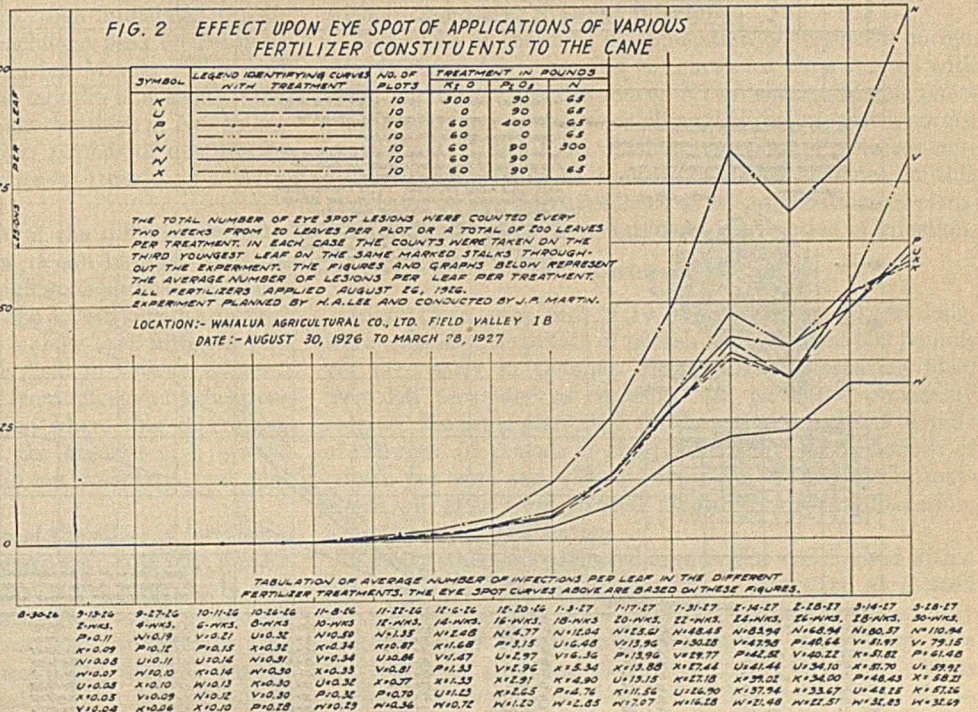
The arrangement of plots in this experiment has already been described and shown in Figure 1. The details concerning the amounts of fertilizers applied are shown in Figure 2. The nitrogen was obtained from nitrate of soda, the phosphoric acid from calcium superphosphate, and the potash from sulfate of potash. The average infection per leaf in the different treatments can be followed in Figure 2.

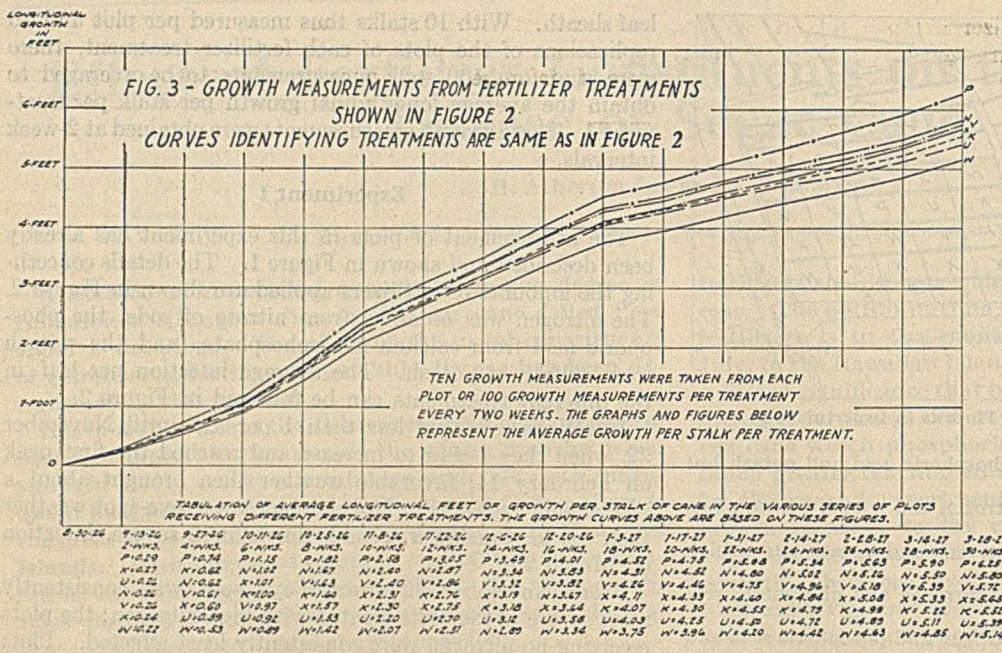
Infections averaged less than 1 per leaf until November 22, when they began to increase and reached the first peak on February 14; favorable weather then brought about a recession in eye spot for 2 weeks; but severe eye-spot weather then set in, causing a second, much more severe, infection on March 28.

From November 22 onward eye spot was consistently most severe in the plots treated with high nitrogen; the plots receiving no nitrogen were consistently least affected. Plots with no nitrogen averaged but 32.8 infections per leaf at the highest peak of infection, which would cause but negligible injury to the cane plant. Plots with 65 pounds of nitrogen per acre averaged 58 infections per leaf or 77 per cent more than the plots with no nitrogen. Plots with 300 pounds of nitrogen per acre averaged 111 infections per leaf, or 238 per cent more than the plots with no nitrogen. It seems established, therefore, that nitrogen applications in the fall months increase eye-spot infection.

In this field, plots with no phosphoric acid had more infection consistently throughout the experiment than the plots with 400 pounds of phosphoric acid per acre, and at the first peak of infection there was 12 per cent more infection in the plots with no phosphoric acid. At the second peak of infection there was 28 per cent more infection in the plots

<sup>2</sup> This method of obtaining growth measurements of sugar cane was developed by Wm. P. Alexander, in charge of the Research Department, Ewa Plantation Co., Ltd., Ewa, T. H.





ences are merely due to chance. Nevertheless, these results should also be kept in mind.

In the growth curves shown in Figure 3 one is surprised to observe that in this field phosphoric acid gave a better growth response to the cane than the nitrogen. The plots treated with 400 pounds of phosphoric acid per acre averaged 7.2 inches more longitudinal growth per stalk than the plots with usual plantation practice (90 pounds  $P_2O_5$  per acre), a very profitable increased yield in 7 months from time of application. The plots with 300 pounds of nitrogen per acre averaged 1.8 inches more longitudinal growth per stalk in 7 months than the usual plantation

having no phosphoric acid than in those having high phosphoric acid. From the results of this experiment alone it would be difficult to say that phosphoric acid applications reduce eye spot, since the differences were not large and might be due to chance. However, it is well to keep in mind these results with phosphoric acid.

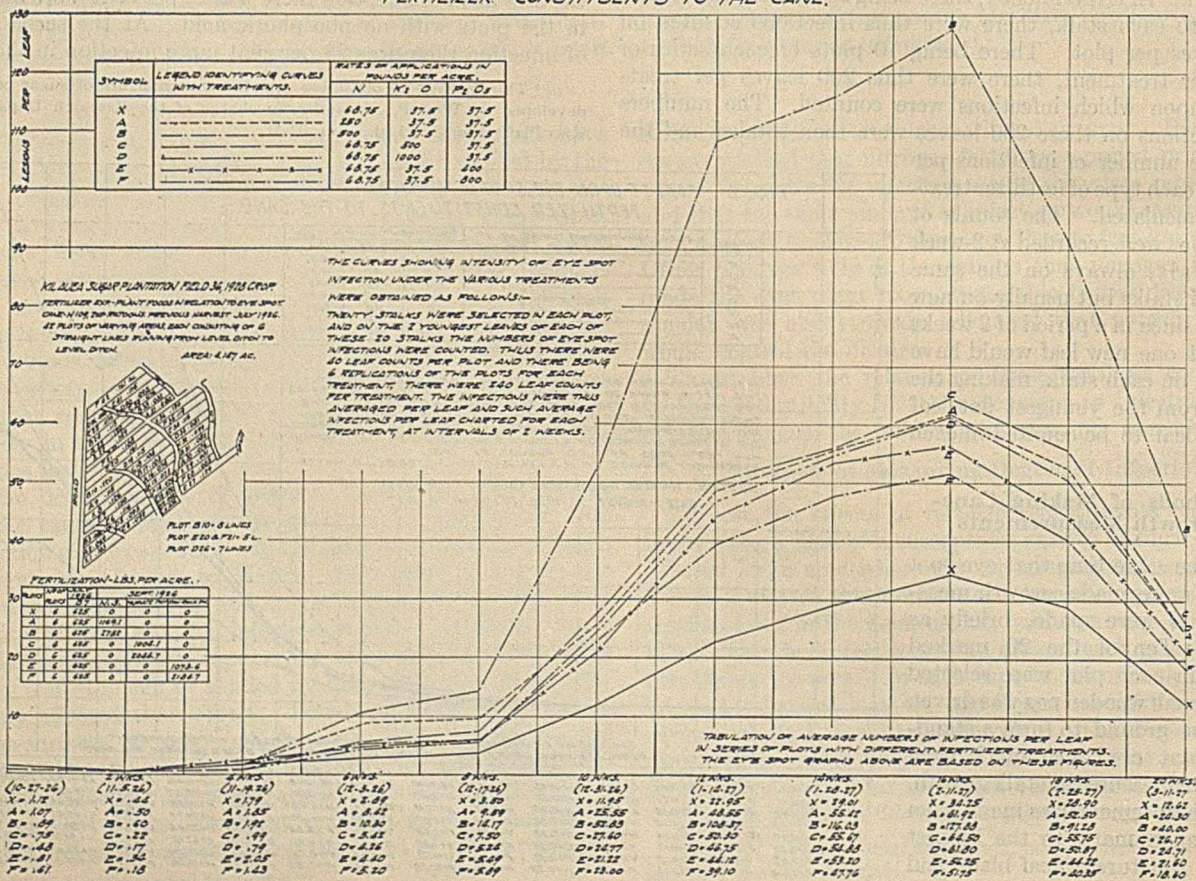
At both high peaks of infection, plots with 300 pounds of potash per acre had slightly less infection per leaf than plots with no potash per acre, but the differences in this case are also so slight that one cannot be sure but that these differ-

practice (65 pounds nitrogen per acre at this application). Potash applications did not increase growth in this field.

Experiment II

In this experiment intensity of eye spot was compared between series of plots of cane treated with very high and moderate applications of the various fertilizers, and plots of usual plantation practice. The fertilizers of usual plantation practice were applied in July, 1926, and the fertilizers with the high rates of application were applied in September,

FIG. 4:- THE EFFECT UPON EYE SPOT OF APPLICATIONS OF THE VARIOUS FERTILIZER CONSTITUENTS TO THE CANE.



1926. In each series of fertilizer treatments there were six replications of plots. The arrangement of the experiment is shown to the left in Figure 4.

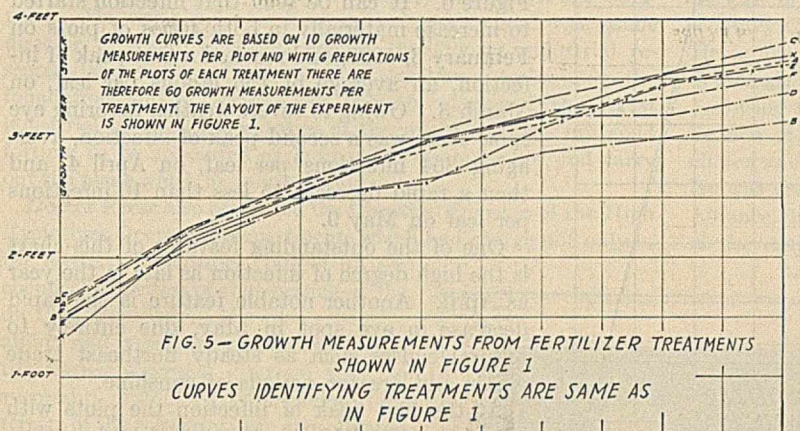


FIG. 5—GROWTH MEASUREMENTS FROM FERTILIZER TREATMENTS SHOWN IN FIGURE 1. CURVES IDENTIFYING TREATMENTS ARE SAME AS IN FIGURE 1.

TABULATION OF AVERAGE GROWTH IN FEET PER STALK OF CANE IN PLOTS WITH DIFFERENT FERTILIZER TREATMENTS. THE GROWTH CURVES ABOVE ARE BASED ON THESE FIGURES.

(10-22-26)	2 WKS. (11-5-26)	4 WKS. (11-19-26)	6 WKS. (12-3-26)	8 WKS. (12-17-26)	10 WKS. (12-31-26)	12 WKS. (1-14-27)
A=1.61	A=2.04	A=2.62	A=2.92	A=3.12	A=3.27	A=3.66
B=1.51	B=2.07	B=2.49	B=2.66	B=2.89	B=3.00	B=3.23
C=1.66	C=2.24	C=2.65	C=3.05	C=3.35	C=3.56	C=3.81
D=1.64	D=2.22	D=2.57	D=2.96	D=3.19	D=3.19	D=3.77
E=1.50	E=2.12	E=2.50	E=2.63	E=3.11	E=3.66	E=3.61
F=1.53	F=2.19	F=2.57	F=2.92	F=3.23	F=3.33	F=3.52
X=1.34	X=2.15	X=2.56	X=2.93	X=3.18	X=3.34	X=3.69

The amounts of the fertilizer constituents applied in September were excessively high, for the purpose of accentuating any differences which might occur in the severity of eye-spot infection resulting from the various treatments. The amounts of such constituents are also shown in the table in Figure 4.

In the case of this test eye-spot counts were made from the first two fully unfolded leaves per stalk, of 20 stalks per plot. Since there were 6 replications of plots for each treatment, there were thus 240 leaf counts of infections for each treatment. Such eye-spot counts were made every 2 weeks. The average infections per leaf in each series of plots of the different fertilizer treatments are charted in Figure 4.

Disregarding for the time being the effect of the different fertilizer treatments on the disease it can be seen from Figure 4 that in this experiment infections averaged less than 3 per leaf up to November 19, 1926, then multiplied rapidly during December and January, reaching a peak on February 11, and then decreasing rapidly during March. This peak of eye-spot infection in the winter months is a usual thing, and is explained naturally by the shorter days in November, December, and January with longer periods of dew on the leaves, and more moisture on the leaves from the more frequent winter rains.

Turning attention to the effect of the different fertilizer constituents on eye-spot infection, it can be seen from the eye-spot graphs in Figure 4 that high applications of nitrogen fertilizers tremendously increased the severity of the disease; yet the growth curves in Figure 5 show that nitrogen produced no growth response in this field in this experiment. The absence of a growth response from nitrogen applications is not uncommon at the plantation where this experiment was conducted. Yet in spite of the absence of a growth response, inorganic nitrogen fertilizers increased eye spot greatly.

The writers' previous conception of the effect of fertilizers, particularly nitrogen, in increasing eye spot, was that a more soft, succulent growth was produced which was highly susceptible. The results of this experiment, showing no growth response from nitrogen applications but an immense eye-spot reaction, alter this conception. The decided growth response from phosphoric acid fertilizers in Experiment I,

with no corresponding increase in eye spot, while nitrogen fertilizers greatly increased infection without so great a growth increase, is in support of these results of Experiment II, indicating that the increase in eye spot following applications of nitrogen fertilizer is not due to soft, more succulent cane. The logical conception at present is that the inorganic nitrogen gets into the cane juices of the leaves and such juices then provide a better medium for the development of the eye-spot fungus than juices without inorganic nitrogen.

From a plantation viewpoint the results of both Experiments I and II indicate that applications of fertilizers containing nitrogen in fields of varieties of cane susceptible to eye spot should be avoided in the later summer and fall months, in order to escape the eye spot response during the winter months of short daylight, longer periods of dew, and greater probabilities of wet leaves from rainfall. In theory, such applications should be made at such a time that the physiological response will occur in May, June, or July, during the period of the greatest length of sunlight, less persistent dew on the leaves, and less chances for rainfall.

In Figure 4 it is seen that the eye-spot response is consistently greater from moderate (curve C) than from large applications of potash (curve D) through most of the period of the experiment. The decreases in eye spot was not great, and possibly is not significant, but at least merits recognition for consideration in connection with subsequent experiments.

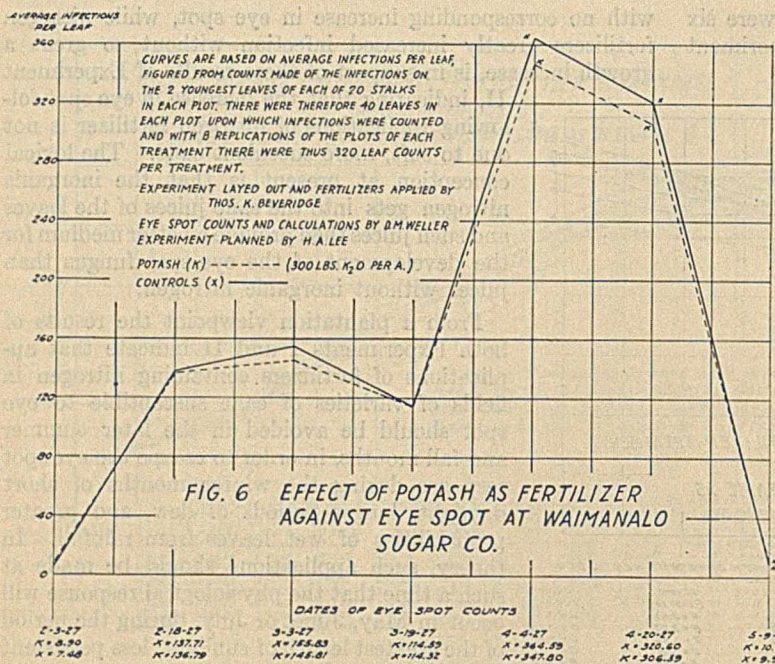
Plots with large applications of phosphoric acid (curve F, Figure 4) also showed less eye spot than plots with more moderate applications (curve E). The difference here is also slight and in itself is of doubtful significance. Similar results in Experiment I suggest that phosphoric acid decreases eye spot slightly. It would be expected that the effect of phosphoric acid and potash fertilizers, if any, on eye spot would vary in different fields of different soil complexes. It can at least be concluded that applications of phosphoric acid and potash fertilizers may produce growth responses, without increasing eye-spot infection.

The effect of the time of application of fertilizers on eye spot is shown by comparing the curve for plots treated with usual plantation practice (curve X) in which nitrogen, phosphoric acid, and potash were all applied in July, with curves A, B, C, D, E, and F, in which applications of fertilizer constituents were made in September. The evidence in this case is very clear that avoidance of late applications of nitrogen fertilizers results in a considerable reduction of infection.

### Experiment III

Eight plots, each plot of 10 rows, each row 30 feet long, were treated with sulfate of potash at the rate of 600 pounds per acre early in October, 1926. Eight alternating plots were left untreated as controls. All plots had previously received the usual plantation fertilizer practice of 185 pounds of nitrogen, 55 pounds of phosphoric acid, and 55 pounds of potash per acre, and with the exception of the potash treatments all plots were treated identically as to cultivation, irrigation, and fertilization.

Twenty stalks were selected in each plot and marked with a red cloth for future identification. Thereafter at 2-week intervals the number of infections on the two youngest fully unfolded leaves of each stalk was counted. Since there were two leaves per stalk and 20 stalks per plot, there were counts made on 40 leaves per plot, and with 8 replications of the



plots of each treatment there were thus 320 leaves counted for each treatment. The numbers of infections were then averaged per leaf from the counts made on these 320 leaves per treatment.

Table I—Average Infections per Leaf during Period of High Infection

PLOT	MARCH 3	MARCH 19	APRIL 4	APRIL 20
1 K	120	41	222	296
2 X	127	76	248	183
3 K	100	54	200	173
4 X	115	100	263	207
5 K	149	211	296	220
6 X	98	66	319	233
7 K	146	67	286	260
8 X	125	85	326	242
9 K	119	81	234	201
10 X	156	161	246	187
11 K	173	141	277	180
12 X	219	69	273	230
13 K	169	70	263	180
14 X	223	97	269	169
15 K	187	76	90	155
16 X	161	91	251	196

The average infections per leaf in the plots treated with potash, and in the untreated plots, throughout the eye-spot season are charted in Figure 6. It can be seen that infection started to increase materially in both series of plots on February 3, 1927, and reached a first peak of infection, an average of 155 lesions per leaf, on March 3. Owing to severe weather favoring eye spot, there was a second peak of infection, averaging 364 infections per leaf, on April 4, and then a rapid decrease to less than 10 infections per leaf on May 9.

One of the outstanding features of this chart is the high degree of infection as late in the year as April. Another notable feature is the rapid decrease in eye spot in May, due entirely to natural causes such as steady northeast trade winds and greater periods of sunshine.

At the first peak of infection the plots with potash averaged 10 infections per leaf less than the plots without potash. At the second peak of infection plots with potash averaged 17 infections per leaf less than those without the potash treatment. One is inclined to question whether this lessened infection is due to chance or actually is brought about by the applications of potash. An analysis of the data at the peaks of infection, as shown in Table I, indicates that the results are fairly consistent as a large proportion of the plots with potash treatment had less average lesions per leaf than the untreated plots. Briefly, most of the alternating plots treated with potash show less eye spot than the plots without potash treatment.

These results in conjunction with the results of Experiments I and II, in which potash applications also reduced eye-spot infection slightly, lead to the belief that such potash applications do definitely lessen infection, at least in the fields in which the tests were conducted. The reduction of infection secured from such treatments was not large, but the difference of 10 or 15 infections per leaf may be the difference between top rot and merely leaf infection; the former resulting in severe injury to the crop, and the latter resulting only in minor injury.

## AMERICAN CONTEMPORARIES

### Charles Lee Reese

I FIRST met Charles Lee Reese in Heidelberg in the fall of 1884. I had been a student there during the summer semester, and in the fall Charles came, fresh from Virginia, to work there under Bunsen. During that winter we began a close friendship, which has lasted ever since. I never shall forget the "teas" we had. After working in the laboratory all day, we would adjourn to my room to drink innumerable cups of tea and discuss all possible subjects.

Charles L. Reese was born in Baltimore, Md., November 4, 1862. He was graduated from the University of Virginia in 1884. He studied abroad at Heidelberg under Bunsen, there receiving the degree of doctor of philosophy in the spring of 1886. He then proceeded to Göttingen to work in organic chemistry under Victor Meyer. Both the University of Pennsylvania and Colgate University conferred on him the honorary degree of doctor of science in 1919, and in 1920 he was made a member of the Phi Beta Kappa society by the University of Virginia.

For fourteen years after his return from Germany in 1886, Doctor Reese was engaged in teaching, first as assistant in chemistry at Johns Hopkins, then as professor of chemistry at Wake Forest College, and later at the South Carolina Military College. While in South Carolina he published a very important paper on the "Origin of Carolina Phosphates," being the first to develop the theory of their formation which is now universally accepted. Later he became instructor in chemistry at Johns Hopkins, where he also published important papers.

Up to the time Doctor Reese left Johns Hopkins University in 1900, his career had been similar to that of hundreds of other chemists in this country who devote their lives to teaching and research, and that date can be said to mark a definite turning-point in his life, for it was then that he started on his technical career, which has led to such brilliant results.

He began this work as chief chemist for the New Jersey Zinc Company. At this time the contact process for sulfuric acid

was in its infancy. Doctor Reese developed this process until it was on a satisfactory working basis, and it was through this work that he drew the attention of the du Pont Company.

In 1902 he was appointed chief chemist of the du Pont Company. He organized the Eastern Laboratory and was made director thereof. This was one of the pioneer industrial research laboratories of the country, and now, built upon the foundations laid by Doctor Reese, it has become one of the largest industrial research laboratories in the world. It was my good fortune to be appointed as Doctor Reese's successor and carry out the plans which he so wisely laid out.

Doctor Reese also organized the Chemical Division of the High Explosives Operating Department, which had charge not only of the Eastern Laboratory, but of all the chemical activities of that branch of the du Pont Company. His rare executive ability and systematic coördination of all the varied chemical interests were so successful that in 1911 the chemical interests of the company were consolidated into a Chemical Department and Doctor Reese was appointed chemical director.

Even before the European war this position was one of great responsibility, for the du Pont Company had begun to branch out from the explosives industry, and at that time employed about four hundred chemists. With the outbreak of the war the responsibilities of this position increased many fold, but Doctor Reese was equal to the emergency. He was always the leader and director in developing new processes and bringing about efficiency in chemical operations when the war made such demands on the nation. When the war shut off the importation of many raw materials, his department developed new processes for making those materials in this country with such promptness that there was no delay in filling orders for military explosives for our allies. During the war the du Pont Company had in its employ as many as twelve hundred chemists at one time.

Since the war the du Pont Company has been engaged in developing the dye industry on a very extensive scale, and in this development the Chemical Department, under Doctor Reese's direction, has played a very important role.

Up to 1921 the Chemical Department of the du Pont Company was composed of five research laboratories: the Experimental Station, devoted to problems on smokeless powder subjects, ballistics, artificial leather, paints and varnishes, etc.; the Eastern Laboratory, devoted principally to work on high explosives; the Jackson Laboratory, to work on dyes; the Delta Laboratory, to work on pyralin, nitrocellulose plastics, etc.; and the Redpath Laboratory, to problems connected with the photographic film industry. There was also a large force of chemical experts at the central office in Wilmington, who devoted their time to the organization and correlation of the work in the laboratories. At the beginning of 1920 there were over four hundred chemists in the Chemical Department of the company. This great organization was built up under the direction of Doctor Reese, and its success is due to his foresight in planning the organization, and his executive ability in carrying out these plans. In recognition of his valuable services he was elected a director of the du Pont Company in 1917.

Doctor Reese is a fellow of the American Association for the Advancement of Science, member of the AMERICAN CHEMICAL SOCIETY, the Society of Chemical Industry, the American Institute of Chemical Engineers, the Franklin Institute, Chemists'

Club of New York, associate member of the Naval Consulting Board and chairman of the Delaware State Committee of that body, member of the Advisory Board of the Chemical Warfare Service of the War Department, member of the Wilmington Country Club, and holds membership in many foreign societies. He is also a member of the Philadelphia Print Club and the Wilmington Sketch Club.

During 1918, Doctor Reese was chairman of the Philadelphia Section of the AMERICAN CHEMICAL SOCIETY and in 1919 was chosen as chairman of the Delaware Section of the same SOCIETY. He was also chairman of the Dyestuffs Section of the Chemical Alliance, Inc. He was appointed chairman of the Dye Section of the AMERICAN CHEMICAL SOCIETY, and in 1920 was elected president of the Manufacturing Chemists' Association of the United States, continuing in that office for three successive years. From 1923 to 1925 he was president of the American Institute of Chemical Engineers. In 1922 he was honored by election to membership in the American Philosophical Society. In 1927 he was elected a director of the AMERICAN CHEMICAL SOCIETY.

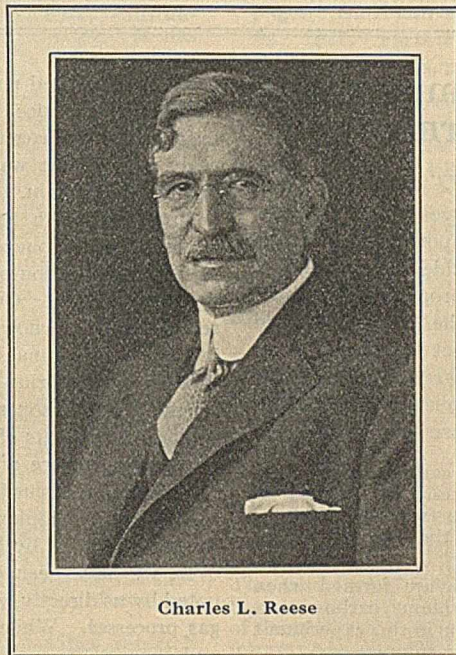
Doctor Reese has always taken an active interest in the affairs of the National Research Council, and in that organization has held the offices of vice chairman of the Division of Chemistry and Chemical Technology, vice chairman of the Research Information Service Division, and is at present a member of the board of trustees of the International Critical Tables of Physical and Chemical Constants. He has recently been elected a counselor of the International Union of Pure and Applied Chemistry.

In Doctor Reese the scientific world has for many years recognized an ardent worker and supporter. Possessed of the broadness of mind and the vision so

necessary in the field of science and research, he has unreservedly lent his time, his talent, and his influence to the support of any projects which had for their object the advancement of science. He was a pioneer in the field of industrial research, and his implicit faith in the accomplishments which may be attained through the application of scientific research to industry has been borne out by the tremendous advances which the industry has made under his direction. While he can review with satisfaction the past accomplishments of scientific research, he is ever looking forward with that same vision to even greater developments in the future.

Doctor Reese has always evidenced a keen interest in his associates. Probably his most outstanding characteristic as an executive is his ability to study men and analyze their capabilities. He possesses that force of character which seems to inspire his men to higher things and broader thinking. His advice to his younger professional associates has never been in the nature of flattery, but has been good, sound advice given with all frankness. On every hand in the organization with which he is connected he can point to men of great accomplishment whom he guided during the period when they were molding their careers.

Another cause of his great success is the extreme fairness of his dealings with the large force of chemists in his department. He delegated more responsibility to those who deserved it than is usual in such organizations, and he was always glad to give every man full credit for what he had done—all of which resulted in his men doing their very best work, and in the greatest harmony in the department and the kindest feeling towards himself.



Charles L. Reese

Although the direction of the Chemical Department has been Doctor Reese's main activity, he has found time to invent a number of processes having a direct bearing on the chemical industry, and for these he has been granted several United States patents.

Matters concerning the cultural side of life have always been a source of great interest to Doctor Reese. Since the beginning of his professional career he has been interested in education and art. He has very definite ideas on educational methods,

especially as regards the training of chemists and chemical engineers, and has on several occasions contributed valuable ideas and advice in this direction. He finds no end of enjoyment in collecting and studying etchings and engravings; he is a lover of books, and has a deep appreciation of the fine arts.

As a scientist, thorough; as an executive, keen; as an educator, uplifting and sympathetic; he has that rare combination of traits which make a builder of character.

ARTHUR M. COMEY

## NOTES AND CORRESPONDENCE

### The Carbon-Sulfur Complex and Carbon Disulfide Formation

*Editor of Industrial and Engineering Chemistry:*

In an interesting paper Huff and Holtz<sup>1</sup> suggest that the formation of a carbon-sulfur complex plays an important part in the origin and decomposition of carbon disulfide in gas-making. They cite my investigation of 1922<sup>2</sup> on the properties of carbon-sulfur complexes and state that "although he (Wibaut) passed sulfur vapors over charcoal he did not detect the formation of carbon disulfide." I wish to point out that this has been the subject of a more extensive investigation, published by me in collaboration with La Bastide in 1924,<sup>3</sup> in which we have shown that:

(1) Carbon disulfide is formed when carbon-sulfur complexes of high sulfur content are decomposed by heating *in vacuo*. The splitting off of carbon disulfide from this carbon-sulfur complex occurs intermittently when the temperature of heating is 600°, 800°, or 1000–1100° C.

(2) Small quantities of carbon disulfide are formed when sulfur vapor is conducted over pure amorphous carbon at a temperature of 600° C. The remaining carbon in this experiment had fixed sulfur in the form of a carbon-sulfur complex.

In 1922<sup>2</sup> I suggested that the formation of a carbon-sulfur complex precedes the formation of carbon disulfide, which is formed by decomposition of the carbon-sulfur complex, and I called attention to the analogy with the behavior of amorphous carbon towards oxygen as revealed by the investigations of Rhead and Wheeler. I believe that the experiments described in my 1924 paper support the hypothesis, which has been proposed independently by Huff and Holtz.

J. P. WIBAUT

UNIVERSITY OF AMSTERDAM  
AMSTERDAM, HOLLAND  
December 20, 1927

these authors used no experimental conditions comparable with commercial practice, unless the treatment of the carbon-sulfur residue with hydrogen gas can be so regarded, and here apparently no attempt was made to detect carbon disulfide in the issuing gas stream. Our investigations,<sup>4</sup> on the other hand, dealt in part with the formation and decomposition of carbon disulfide on carbonaceous surfaces when these surfaces are subjected to the action of gas streams containing small amounts of hydrogen sulfide. Our experiments showed, for the first time to our present knowledge, that under conditions encountered in the usual gas-making practice there may be, and often is, a definite period during which decomposition with sulfur deposition on the fresh carbon surfaces occurs without the appearance of detectable amounts of carbon disulfide, and that this is followed by the appearance of carbon disulfide in the gaseous products.

This appears to us to establish for the first time the role of the carbon-sulfur complex and the mechanism in gas-making similar to that visualized by Rhead and Wheeler in combustion. Moreover, we have been able to link the experimental phenomena noted by us directly with published information upon commercial gas processes. While we are glad to cite ancillary information and suggestions such as those of Wibaut and La Bastide, and had no wish to do otherwise than accord just credit, it appears to us that Wibaut can hardly claim priority for the suggestion that a complex may appear in the reaction between carbon and sulfur to form carbon disulfide, since this suggestion was made in 1915 by Lewis and Lacey,<sup>5</sup> as noted in our paper.

We therefore see at present no reason for modifying the statements made in our contribution.

WILBERT J. HUFF  
JOHN C. HOLTZ

THE DEPARTMENT OF GAS ENGINEERING  
JOHNS HOPKINS UNIVERSITY  
BALTIMORE, MD.  
January 5, 1928

<sup>1</sup> *Ind. Eng. Chem.*, **18**, 357 (1926); **19**, 1268 (1927).

<sup>2</sup> *J. Am. Chem. Soc.*, **37**, 1976 (1915).

### Lignin Has Industrial Value

Several years ago the chemists of the Department of Agriculture undertook to salvage some of the value of agricultural wastes, such as corn cobs, corn stalks, and straw, and in the course of time evolved processes for the manufacture of furfural which is now being used for many purposes. As soon as its commercial possibilities were assured, the Government discontinued the furfural experiments and commercial interests took over the work.

Lignin constitutes from 20 to 30 per cent of the dry material of these wastes. Chemists have already succeeded in converting lignin into varnishes, dyestuffs, and various aromatic chemicals that give promise of finding their place in the commercial chemical field. "Lignin," says Doctor Browne, assistant chief of the Bureau of Chemistry and Soils, "may be called the greatest of all unutilized agricultural wastes," and he continues with the significant statement that "it occupies with respect to industrial possibilities the position held by coal tar a century ago."

*Editor of Industrial and Engineering Chemistry:*

As noted by Wibaut, our statement concerning his work was made with reference to his investigation of 1922, and is correct. At the time our own paper was written we had not seen the later results of Wibaut and La Bastide and are happy to make mention of these, which are not at variance with our independent conclusions.

We do not, however, regard the work of these authors as an anticipation of our own. The problem under study by us was the "Origin and Decomposition of Carbon Disulfide in Gas-Making." So far as we are aware, the long treatment of carbon with pure sulfur and decomposition *in vacuo* used by Wibaut and La Bastide is not encountered in commercial gas-making, and

<sup>1</sup> *Ind. Eng. Chem.*, **19**, 1268 (1927).

<sup>2</sup> *Rec. trav. chim.*, **41**, 153 (1922).

<sup>3</sup> *Ibid.*, **43**, 731 (1924).

## BOOK REVIEWS

**Annual Survey of American Chemistry—Vol. II.** Edited by CLARENCE J. WEST under the auspices of the Division of Chemistry and Chemical Technology of the National Research Council. 415 pages. The Chemical Catalog Company, Inc., New York, 1927. Price, \$3.00.

The growth of this review, first undertaken last year, from 34 chapters of 257 pages in Volume I to 49 chapters of 415 pages, with 51 contributors, in Volume II, is evidence that it has established its value as a part of chemical literature and as a substantial aid to the development of chemistry in America. It has immediately won a place as a prominent activity of the Division of Chemistry and apparently will be recognized as one of the important undertakings of the Research Council. Doctor Hale is to be congratulated upon its initiation and the Council upon having the services of Doctor West to carry it on as a continuous project.

The policy of not adhering to all of the same subjects each year is a wise one, which insures adequate representation of various fields by distributing them over a term of years. The addition of an author's index is very welcome, and partial compensation for this lack in the first volume is made by including both in the second. It is apparent, however, that author's initials, at least, should be given, in the index.

One possible objection to such a review is that in being confined to American work it must be too narrow and have little comprehensive value. The volume appears to answer this criticism in a most direct way. While it is impossible to include the world literature, ready access to it can be had by referring to the papers cited and a picture of world progress is skilfully interwoven with the account of the American work in each field. The purpose of the review, however, is not to vaunt American chemistry, but rather to stimulate it by presenting its annual achievements and thus afford a basis of comparison internally and externally. Statistical comparison with the outside literature in a given field, such as Mr. Fieldner has made for his subject, is useful and in many cases should have both a chastening and stimulating effect.

The contributors are distributed between universities, research institutions, and industry, thus giving suitable representation to both science and technology. It will require judgment and sound selection to maintain a proper balance between them, but by judicious use of alternation no difficulty in this respect should be encountered.

While doubtless some important work has been omitted from review through its failure to fall into one of the adopted classes, to the reviewer the survey seems to have been made with great thoroughness and outstanding ability. These comprehensive pictures of the present status and progress in each field cannot fail to have a most stimulating influence in chemical science and technology, not only in America but abroad.

S. C. LIND

**Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colors.** By HENRY A. GARDNER. 4th edition. 765 pages with a 261-page appendix of U. S. Government Specifications. 300 figures. Institute of Paint and Varnish Research, Washington, D. C., 1927. Price, \$11.00.

Previous editions of this book have been revised and greatly enlarged in order to bring all the material up to date. The methods for testing and analysis are those in actual use at the present time and they are clearly written and thoroughly discussed. Numerous specifications add to the value of the book.

Approximately half of the manual is devoted to a comprehensive discussion of physical testing, contained in 22 chapters. The following topics will be of especial interest: hiding power, brightness, particle size of pigments, ultra-violet light studies, surface tension, tensile strength. Two chapters on the analysis and testing of lacquers are well written considering the present state of development.

Like the earlier editions, this book will be exceedingly valuable to laboratory workers in the paint and varnish industry. The chapters upon physical testing will be of great help to research workers in this field.

The chief criticism of this edition is the lack of a logical arrange-

ment of the topics discussed. It is also too large for convenient use in a laboratory. It is hoped that future editions will appear in two volumes, one devoted to a general discussion of physical testing, arranged in a more logical order, and a second, to routine testing and methods of analysis.

W. T. PEARCE

**A. S. T. M. Standards (Issued Triennially), 1927. Part I—Metals.** 878 pages. Part II—Non-Metallic Materials. 1006 pages. American Society for Testing Materials, Philadelphia, Pa., 1927. Parts I and II, each, cloth, \$7.50; half-leather, \$9.00; both parts, cloth, \$14.00; half-leather, \$17.00.

The 1927 edition of the Triennial Standards of the American Society for Testing Materials contains 340 standard specifications, methods of tests, definitions of terms, and recommended practices. Part I contains 144 standards relating to metals, whereas Part II has 196 standards on non-metallic materials. Before a standard receives the official approval of the society, it is published for one or more years as a tentative standard. Criticisms of such tentative standards are solicited and all suggestions are given careful consideration before final adoption is recommended. These standards are recognized as authoritative in the field of engineering materials.

**Industrial Research Laboratories of the United States, Including Consulting and Research Laboratories.** Compiled by CLARENCE J. WEST and ERVYE RISCHER. *Bulletin* 60, National Research Council. 3rd edition, revised and enlarged. 153 pages. National Research Council, Washington, 1927. Price, \$1.00.

The present bulletin contains data on 1000 laboratories, as contrasted with 526 in the second and 300 in the initial edition. The laboratories are listed alphabetically and are followed by the addresses of directors of research, geographical distribution of laboratories, and finally, their subject classification. The information has been gathered by direct correspondence with the industrial and consulting research laboratories, and notwithstanding the size of this list, it is not complete, inasmuch as some concerns did not answer inquiries, while in a few cases they declined to be included. Laboratories connected with the federal, state, or municipal governments or with educational institutions have not been included, nor have the associations and concerns supporting research in laboratories other than their own, if in such cases they do not support a laboratory in their own works.

The list is very informative and remarkably full in detail when the difficulty of collecting such data is appreciated. It reflects the present status of industrial research in the United States and brings together in convenient form details as to research staff and research work in so wide a variety of industries as to prove an invaluable reference work.

**Die Neueren Milchindustrien. Technische Fortschrittsberichte. Fortschritte der Chem. Technologie in Einzeldarstellungen. Band XIV.** By L. EBERLEIN. 119 pages. Theodor Steinkopf, Dresden and Leipzig, 1927. Price, paper, 5 marks; bound, 6.20 marks.

The book is one of a series of technical reports of progress in various fields. It is an attempt to give the latest and best results in the field of dairy science since 1914 in the form of a review suitable for physicians, veterinarians, and other technical men. The book is more than a review of subjects, in that certain chemical and bacteriological aspects are discussed. The citations of literature in the purely scientific phases are not so complete as in those dealing with the industrial aspects.

The subjects discussed are (1) preservation of milk; (2) industrial, chemical, and bacteriological aspects of condensation of milk; (3) drying of milk; (4) milk preparations; (5) casein; (6) milk sugar. Discussions accompanying the last three subjects are of especial interest to American readers in that they embody much of the foreign literature.

GEORGE E. HOLM

# 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

Foreign Commerce and Navigation of the United States for the Calendar Year 1926. In Two Volumes. Volume I. 543 pp. Cloth, \$1.75.  
World-Wide Importance of United States Chemical Industry: United States Produces \$2,278,000,000 Worth of Chemicals. A. H. SWIFT. 7 pp. Reprinted from *Commerce Reports*, December 12, 1927.

## Bureau of Mines

Abrasive Materials in 1926. *Mineral Resources of the United States, 1926*. Part II, pp. 245-53. Paper, 5 cents.  
Asbestos in 1926. B. H. STODDARD. *Mineral Resources of the United States, 1926*. Part II, pp. 195-201. Paper, 5 cents.  
Consumption of Explosives in November, 1927. W. W. ADAMS. *Reports of Investigations* 2845. 9 pp.  
Development of Some Fundamentals in the Ferric Sulfate-Sulfuric Acid Process. F. S. WARTMAN AND H. E. KEYES. *Reports of Investigations* 2839. 11 pp.  
Lead and Zinc Pigments and Salts in 1926. A. STOLL. *Mineral Resources of the United States, 1926*. Part I, pp. 217-26. Paper, 5 cents.  
Mica in 1926. B. H. STODDARD. *Mineral Resources of the United States, 1926*. Part II, pp. 255-71. Paper, 5 cents.  
Mineral Resources of the United States, 1924. Part I—Metals. 589 pp. Cloth, \$1.00. Part 2—Nonmetals. 728 pp. Cloth, \$1.00.  
National Survey of Fuel Oil Distribution, 1926. E. B. SWANSON. A Report of the U. S. Bureau of Mines, Department of Commerce, in Cooperation with the American Petroleum Institute. 22 pp.  
Petroleum, Petroleum Products, and Natural-Gas Gasoline, January, 1928. *Statistical and Economic Surveys. Monthly Petroleum Statement* P 31. 11 pp.  
Phosphate Rock in 1926. *Mineral Resources of the United States, 1926*. Part II, pp. 273-80. Paper, 5 cents.  
Prevention of Hydrogen Sulfide Poisoning in Handling and Refining High-Sulfur Petroleum. H. C. FOWLER. *Reports of Investigations* 2847. 27 pp.  
Talc and Soapstone in 1926. B. H. STODDARD. *Mineral Resources of the United States, 1926*. Part II, pp. 203-9. Paper, 5 cents.  
The Sulfur Content of Commercial Motor Fuels. A. J. KRAEMER, E. C. LANE, AND C. S. LUCE. *Reports of Investigations* 2843. 8 pp.  
Zinc in 1926 (Smelter Report). AMY STOLL. *Mineral Resources of the United States, 1926*. Part I, pp. 227-47. Paper, 5 cents.

## Bureau of Standards

Cleaning of Fur and Leather Garments. M. H. GOLDMAN AND C. C. HUBBARD. *Technologic Paper* 360. 15 pp. Paper, 10 cents.  
Deterioration of Steels in Synthesis of Ammonia. J. S. VANICK, W. W. DE SVESHNIKOFF, AND J. G. THOMPSON. *Technologic Paper* 361. 35 pp. Paper, 15 cents.  
Elimination of Waste. White Glazed Tile and Unglazed Ceramic Mosaic, 1927. *Simplified Practice Recommendation* 61. Effective January 1, 1927. 28 pp. Paper, 10 cents.  
Gases in Metals. III—The Determination of Nitrogen in Metals by Fusion in Vacuum. LOUIS JORDAN AND J. R. ECKMAN. *Scientific Paper* 563. 19 pp. Paper, 10 cents.  
Thermal Expansion of Beryllium and Aluminum-Beryllium Alloys. PETER HIDNERT AND W. T. SWEENEY. *Scientific Paper* 565. 13 pp. Paper, 10 cents.  
United States Government Master Specification for Ink, Marking, Indelible, for Fabrics. *Circular* 197. 4 pp. Paper, 5 cents.

## Department of Agriculture

A Comparative Study of the Quinhydrone and Hydrogen Electrodes for Determining the Hydrogen-Ion Concentration of Soils. E. F. SNYDER. *Journal of Agricultural Research*, 35 (November 1, 1927), 825-34.  
Definitions and Standards for Food Products. *Service and Regulatory Announcements. Food and Drug* 2. (Supersedes Office of the Secretary Circulars 13, 17, 19, and 136.) 20 pp. Paper, 5 cents.  
Fertilizer Tests with Flue-Cured Tobacco. E. G. MOSS, J. E. MCMURTREY, JR., W. M. LUNN, AND J. M. CARR. *Technical Bulletin* 12. 59 pp. Paper, 15 cents.  
Regulations for the Enforcement of the Caustic Poison Act. *Service and Regulatory Announcement. Caustic Poison* 1. 12 pp. Paper, 5 cents.

Relation between Water and Potash in Plant Production. F. W. MORSE. *Journal of Agricultural Research*, 35 (November 15, 1927), 939-46.  
Report of the Chief of the Bureau of Animal Industry for the Fiscal Year 1927. 50 pp.  
Report of the Chief of the Bureau of Dairy Industry for the Fiscal Year 1927. 16 pp.  
Report of the Chief of the Bureau of Plant Industry for the Fiscal Year 1927. 43 pp.  
The Production of Certain Enzymes by *Bacterium pruni*. S. L. JODIDI. *Journal of Agricultural Research*, 35 (August 1, 1927), 219-21.  
The Relation of Atmospheric Humidity to the Deterioration of Evaporated Apples in Storage. C. W. CULPEPPER AND J. S. CALDWELL. *Journal of Agricultural Research*, 35 (November 15, 1927), 889-906.  
The Resistance of Certain Varieties of Winter Wheat to Artificially Produced Low Temperatures. D. D. HILL AND S. C. SALMON. *Journal of Agricultural Research*, 35 (November 15, 1927), 933-7.  
The Supplementary Relation between the Proteins of Corn and of Tankage Determined by Metabolism Experiments on Swine. H. H. MITCHELL AND C. H. KICK. *Journal of Agricultural Research*, 35 (November 1, 1927), 857-64.

## Geological Survey

Annual Report of the Director of the Geological Survey to the Secretary of the Interior for Fiscal Year Ended June 30, 1927. 77 pp.  
Mineral Industry of Alaska in 1926 and Administrative Report. P. S. SMITH. *Bulletin* 797-A. 66 pp.

## Interstate Commerce Commission

Report of Director of Bureau of Safety to Interstate Commerce Commission for the Fiscal Year 1927, and Extracts from the 41st Annual Report of the Interstate Commerce Commission Pertaining to Safety Appliances, Hours of Service, Medals of Honor, Investigation of Accidents, and Investigation of Safety Devices. 48 pp. Paper, 5 cents.

## Navy Yard

Safety Standards for the Protection of the Head, Eyes, and Respiratory Organs. Paper, 15 cents.

## Public Health Service

A Report on the Disposal of Zyklon-B Residue Following the Fumigation of the Holds of Vessels. G. C. SHERRARD. *Public Health Reports*, 42 (December 16, 1927), 3071-5.  
Benzocaine-Chaulmoogra Oil in the Treatment of Leprosy. Preliminary Note on the Use of an Oil-Soluble Analgesic Which Renders Intramuscular Injections of Chaulmoogra Oil Painless. F. A. JOHANSEN. *Public Health Reports*, 42 (December 9, 1927), 3005-10.  
Shellfish Sanitation. L. M. FISHER. *Public Health Reports*, 42 (September 16, 1927), 2291-300.

## Smithsonian Institution

Report of United States Regional Bureau of International Catalogue of Scientific Literature under Direction of the Smithsonian Institution for the Year Ended June 30, 1927. From the *Smithsonian Report for 1927*. 115 pp.  
The Effect of Aluminum Sulfate on Rhododendrons and Other Acid-Soil Plants. F. V. COVILLE. *Publication* 2897 from the *Smithsonian Report for 1926*, pp. 369-82.

## Treasury Department

Annual Report of the Commissioner of Prohibition for the Fiscal Year 1927. *Department Document* 2988. 92 pp. Paper, 15 cents.

## New Books

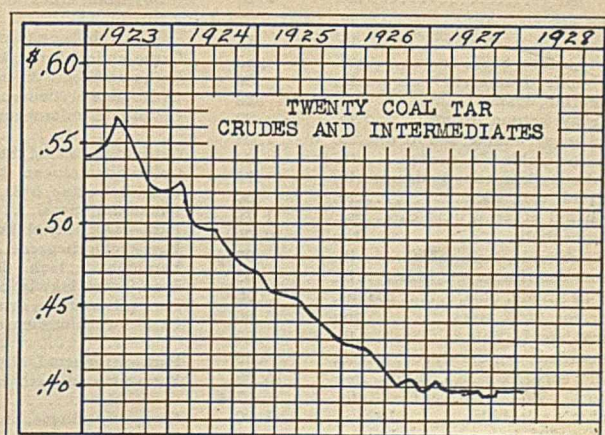
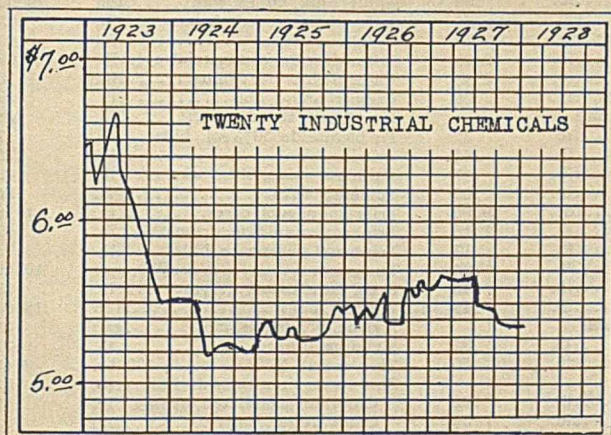
Agenda Chimie, à l'Usage des Chimistes, Ingénieurs, Industriels, Professeurs, Pharmaciens, Directeurs, et Contremaitres d'Usines. EMILE JAVET. Agendas Dunod, 1928. 285 pp. Dunod, Paris. Price, 17 francs.  
Chemical Elements and Their Compounds. An Introduction to the Study of Inorganic Chemistry from Modern Standpoints. J. A. V. BUTLER. 205 pp. The Macmillan Co., New York. Price, \$2.00.  
Elementary Account of the P. E. C. or the Softening of Refractories by Heat. STUART M. PHELPS. *Bulletin* 17, American Refractories Institute, Pittsburgh, Pa.  
Pozzolanas. A. D. COWPER AND F. L. BRADY. *Building Research Bulletin* 2, Department of Scientific and Industrial Research 10 pp. H. M. Stationery Office, London. Price, 3 d. net.



# MARKET REPORT—JANUARY, 1928

FIRST-HAND PRICES FOR CHEMICALS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET ON JANUARY 15

Acetanilide, tech., bbls.....lb.	23	Sulfuric, 66°, c/l. cbys., wks.	1.35	Sulfate, bulk, wks.....100 lbs.	2.40
Acetic anhydride, 92-95%, cbys..lb.	29	66°, tanks, wks.....ton	15.00	Thiocyanate, tech., kegs.....lb.	.40
Acetone, C. P., drums, wks.....lb.	.13	60°, tanks, wks.....ton	10.50	Amyl acetate, tech., drums.....gal.	1.90
Acetophenetidine, bbls.....lb.	1.50	Oleum, 20%, tanks, wks...ton	18.00	Aniline oil, drums.....lb.	.15½
Acid, Acetic, 28%, c/l. bbls.100 lbs.	3.38	40%, tanks, wks.....ton	42.00	Anthracene, 80-85%, casks, wks..lb.	.60
56%, c/l. bbls.....100 lbs.	6.34	Sulfurous, U. S. P., 6%, cbys. lb.	.05	Anthraquinone, subl., bbls.....lb.	.90
Glacial, c/l. bbls.....100 lbs.	11.92	Tannic, tech., bbls.....lb.	.30	Antimony, metal.....lb.	.11½
Acetylsalicylic, bbls.....lb.	.85	Tartaric, U. S. P., cryst.,		Antimony chloride, anhyd.,	
Anthraniic, 99-100%, drums..lb.	.98	bbls.....lb.	.34½	drums.....lb.	.17
Benzoic, tech., bbls.....lb.	.57	Tungstic, kegs.....lb.	1.00	Oxide, bbls.....lb.	.16½
Boric, bbls.....lb.	.08½	Valeric, C. P., 10-lb. bot.....lb.	2.50	Salt, Dom., bbls.....lb.	.18
Butyric, 60%, pure, 5-lb. bot..lb.	.55	Alcohol, U. S. P., 190 proof,		Sulfide, crimson, bbls.....lb.	.25
Chloroacetic, mono, bbls.,		bbls.....gal.	3.70	Golden, bbls.....lb.	.16
wks.....lb.	.25	Amyl, 10%, Imp. drums.....gal.	1.40	Vermilion, bbls.....lb.	.38
Di-, cbys.....lb.	1.00	Butyl, drums, c/l., wks.....lb.	.19½	Tartrolactate, bbls.....lb.	.45
Tri-, bbls.....lb.	2.50	Cologne Spirit, bbls.....gal.	3.90	Argols, red powder, bbls.....lb.	.08
Chlorosulfonic, drums, wks....lb.	.15	Denatured, No. 5, Comp. de-		Arsenic, metal, kegs.....lb.	.45
Chromic, pure, 98%, drums....lb.	.37	nat. c/l, drs.....gal.	.48	Red, kegs, cases.....lb.	.10½
Cinnamic, 5-lb. cans.....lb.	3.25	No. 1, Comp. denat., drs..gal.	.52	White, c/l. kegs.....lb.	.03½
Citric, U. S. P., kegs, bbls....lb.	.44	Isoamyl, drums.....gal.	2.50	Asbestine, bulk, c/l.....ton	14.75
Cresylic, pale, drums.....gal.	.72	Isobutyl, ref., drums.....lb.	...	Barium carbonate, bbls., bags,	
Formic, 85%, cbys., N. Y.....lb.	.11	Isopropyl, ref., drums.....gal.	1.00	wks.....ton	47.00
Gallic, U. S. P., bbls.....lb.	.74	Propyl, ref., drums.....lb.	1.00	Chloride, bags, wks.....ton	55.50
Glycerophosphoric, 25%, 1-		Wood, see Methanol		Dioxide, bbls., wks.....lb.	.13
lb. bot.....lb.	1.40	Alpha-naphthol, bbls.....lb.	.65	Hydroxide, bbls.....lb.	.04½
H, bbls., wks.....lb.	.57	Alpha-naphthylamine, bbls...lb.	.35	Nitrate, casks.....lb.	.07½
Hydriodic, 10%, U. S. P., 5-		Alum, ammonia, lump, bbls.,		Barium sulfocyanate, 400-lb.	
lb. bot.....lb.	.67	wks.....100 lbs.	3.25	bbls.....lb.	.27
Hydrobromic, 48%, cbys., wks.lb.	.45	Chrome, casks, wks.....100 lbs.	5.25	Barytes, floated, 350-lb. bbls.,	
Hydrochloric, 20°, tanks,		Potash, lump, bbls., wks. 100 lbs.	3.10	wks.....ton	23.00
wks.....100 lbs.	1.05	Soda, bbls., wks.....100 lbs.	3.75	Benzaldehyde, tech., drums....lb.	.65
Hydrofluoric, 30%, bbls., wks..lb.	.06	Aluminum, metal, N. Y.....lb.	.26	F. F. C., cbys.....lb.	1.40
60%, bbls., wks.....lb.	.13	Aluminum chloride, anhyd,		U. S. P., cbys.....lb.	1.15
Hydrofluosilicic, 35%, bbls.,		drums.....lb.	.35	Benzene, pure, tanks, mills....gal.	.21
wks.....lb.	.11	Aluminum stearate, 100-lb. bbl..lb.	.23	Benzidine base, bbls.....lb.	.70
Hypophosphorus, 30%, U.		Aluminum sulfate, comm'l,		Benzoyl chloride, carboys.....lb.	1.00
S. P., 5-gal. demis.....lb.	.36	bags, wks.....100 lbs.	1.40	Benzyl acetate, cbys.....lb.	1.30
Lactic, 22%, dark, bbls.....lb.	.05½	Iron-free, bags, wks.....100 lbs.	1.75	Alcohol, 5-liter bot.....lb.	1.40
66%, light, bbls., wks.....lb.	.26	Aminoazobenzene, 110-lb. kgs..lb.	1.15	Chloride, tech., drums.....lb.	.25
Mixed, tanks, wks.....N unit	.07½	Ammonia, anhydrous, cyl., wks..lb.	.14	Beta-naphthol, bbls.....lb.	.24
S unit	.01	Ammonia water, 26°, drums,		Beta-naphthylamine, bbls.....lb.	.63
Molybdic, 85%, kegs.....lb.	1.25	wks.....lb.	.03	Bismuth, metal, cases.....lb.	2.00
Naphthionic, tech., bbls.....lb.	.55	Ammonium acetate, kegs.....lb.	.34	Bismuth nitrate, 25-lb. jars....lb.	1.85
Nitric, C. P., cbys.....lb.	.12	Bifluoride, bbls.....lb.	.21	Oxychloride, boxes.....lb.	3.10
Nitric, 38°, c/l. cbys., wks.		Bromide, 50-lb. boxes.....lb.	.48	Subnitrate, U. S. P., 25-lb.	
.....100 lbs.	5.00	Carbonate, tech., casks.....lb.	.08½	jars.....lb.	2.20
Oxalic, bbls., wks.....lb.	.11	Chloride, gray, bbls..... 100 lbs.	5.40	Blanc fixe, dry, bbls.....ton	80.00
Phosphate, bulk.....ton	9.00	Lump, casks.....lb.	.11	Bleaching powder, drums, wks.	
Phosphoric, 50%, cbys.....lb.	.08	Iodide, 25-lb. jars.....lb.	5.20	.....100 lbs.	2.00
Picramic, bbls.....lb.	.50	Nitrate, tech., cryst., bbls....lb.	.21	Bone ash, kegs.....lb.	.06
Pieric, bbls. c/l.....lb.	.30	Oxalate, kegs.....lb.	.35	Bone black, bbls.....lb.	.08½
Pyrogallic, tech., bbls.....lb.	.86	Persulfate, cases.....lb.	.27½	Borax, powd., bbls.....lb.	.04½
Salicylic, tech., bbls.....lb.	.37	Phosphate, dibasic, tech.,		Bordeaux mixture, bbls.....lb.	.11
Stearic, d. p., bbls. c/l.....lb.	.11½	bbls.....lb.	.18	British gum, com., c/l..... 100 lbs.	4.37
Sulfanilic, 250-lb. bbls.....lb.	.15			Bromine, bot.....lb.	.47
				Bromobenzene, drums.....lb.	.50



Bromoform, 5-lb. bot.....lb.	1.65	G salt, bbls.....lb.	.50	Paris Green, 500-lb. kgs.....lb.	.19
Butyl acetate, 100-gal. drums...gal.	1.55	Hexamethylenetetramine, tech., drums.....lb.	.62	Phenol, drums.....lb.	.17
Cadmium bromide, 50-lb. jars.....lb.	1.20	Hydrogen peroxide, 25 vol., bbls.....lb.	.06½	Phenolphthalein, drums.....lb.	1.10
Cadmium metal, boxes.....lb.	.70	Hydroquinone, kegs.....lb.	1.25	Phenylethyl alcohol, 1-lb. bot.....lb.	7.00
Cadmium sulfide, cs.....lb.	1.35	Indigo, 20%, paste, bbls.....lb.	.14	Phosphorus, red, cases.....lb.	.60
Caffeine, U. S. P., 5-lb. cans.....lb.	3.05	Iodine, crude, 200-lb. kgs.....lb.	4.20	Phosphorus trichloride, cyl.....lb.	.45
Calcium acetate, bags.....100 lbs.	3.50	Iodine, resubl. jars.....lb.	4.65	Phthalic anhydride, bbls.....lb.	.18
Arsenate, bbls.....07½		Iodoform, bot.....lb.	6.00	Platinum, metal.....oz.	95.00
Carbide, drums.....lb.	.05	Iridium, metal.....oz.	110.00	Potash, caustic, drums.....lb.	.07½
Chloride, drums, wks.....ton	21.00	Kieselguhr, bags.....ton	60.00	Potassium acetate, kegs.....lb.	.29
Cyanide, 100-lb. drum.....lb.	.30	Lead, metal.....100 lb.	6.25	Bicarbonate, casks.....lb.	.09
Lactate, tech., bbls.....lb.	.35	Lead acetate, bbls., white.....lb.	.13	Bichromate, casks.....lb.	.08½
Nitrate, bbls.....ton	52.00	Arsenate, bbls.....lb.	.13½	Binodate, bbls.....lb.	.16
Phosphate, monobas., bbls.....lb.	.07	Oxide, litharge, bbls.....lb.	.08¾	Bromate, cs.....lb.	.35
Tribas., bbls.....lb.	.11	Red, bbls.....lb.	.09¾	Carbonate, 80-85%, calc., casks.....lb.	.05½
Calcium carbonate, tech., bgs, 100 lbs.	1.00	Peroxide, drums.....lb.	.25	Chlorate, kegs.....lb.	.08½
U. S. P., precip., 175-lb. bbl.....lb.	.06½	White, basic carb., bbls.....lb.	.09	Chloride.....ton	34.55
Camphor, Amer., bbls.....lb.	.62	Sulfate, bbls.....lb.	.08½	Cyanide, cases.....lb.	.55
Jap., cases.....lb.	.60	Lime, hydrated, bbls.....100 lbs.	.85	Meta-bisulfite, bbls.....lb.	.11
Camphor, monobrom, cs.....lb.	1.85	Lime, live, chemical, bbls., wks. ....100 lbs.	1.05	Permanganate, drums.....lb.	15¼
Caramel, bbls.....gal.	.63	Limestone, ground, bags, wks. ....ton	4.50	Prussiate, red, casks.....lb.	.39
Carbazole, bbls.....lb.	.15	Lithopone, bbls.....lb.	.06½	Yellow, casks.....lb.	.18
Carbon, activated, drums.....lb.	.05	Magnesite, crude.....ton	36.00	Titanium oxalate, bbls.....lb.	.25
Carbon bisulfide, drums.....lb.	.05½	Calcined, 500-lb. bbls., wks. ....ton	48.00	Pyridine, drums.....gal.	1.50
Carbon black, cases.....lb.	.12	Magnesium, metal sticks, wks. ....lb.	.85	Quinine bisulfate, 100 oz.....oz.	.40
Carbon dioxide, liq., cyl.....lb.	.06	Magnesium carbonate, bags.....lb.	.06	Sulfate, 100-oz. cans.....oz.	.40
Carbon tetrachloride, drums.....lb.	.07	Chloride, drums.....ton	37.00	Resorcinol, tech., kegs.....lb.	1.30
Casein, stand. gr., bbls.....lb.	.18½	Fluossilicate, cryst., bbls.....lb.	.10	Rochelle salt, bbls., U. S. P.....lb.	.23
Cellulose acetate, kegs.....lb.	1.40	Oxide, U. S. P., light, bbls.....lb.	.42	R salt, bbls.....lb.	.45
Cerium oxalate, kegs.....lb.	.32	Manganese chloride, casks.....lb.	.08	Saccharin, cans.....lb.	1.75
Charcoal, willow, powd., bbls.....lb.	.06	Dioxide, 80%, bbls.....ton	80.00	Salt cake, bulk.....ton	19.00
China clay, imp., bgs.....100 lbs.	15.00	Sulfate, casks.....lb.	.07	Saltpetr, gran., bbls.....lb.	.06
Chloral hydrate, drums.....lb.	.60	Mercury bichloride, cryst., 25 lbs.lb.	1.58	Silica, ref., bags.....ton	18.00
Chloramine U. S. P., 5-lb. bot.....lb.	1.75	Mercury, flasks, 75 lbs.....flask	126.00	Silver nitrate, 16-oz. bot.....oz.	41½
Chlorine, liq., c/l., cyl.....lb.	.04	Meta-nitroaniline, bbls.....lb.	.72	Soda ash, 58%, light, bags, contract, wks.....100 lbs.	1.40
Chlorobenzene, mono, drums.....lb.	.07	Meta-phenylenediamine, bbls.....lb.	.90	Soda, caustic, 76%, solid, drums, contract, wks.....100 lbs.	3.00
Chloroform, tech., drums.....lb.	.20	Meta-toluylenediamine, bbls.....lb.	.72	Sodium acetate, bbls.....lb.	.04½
Chromium acetate, 20° sol., bbls.lb.	.05½	Methanol, pure, tanks.....gal.	.50	Benzoate, bbls.....lb.	.50
Coal tar, tanks, bbls., wks.....gal.	.07	Denaturing grade, tanks.....gal.	.75	Bicarbonate, bbls.....100 lbs.	2.00
Cobalt, metal, kegs.....lb.	2.50	Methyl acetone, drums.....gal.	.80	Bichromate, casks.....lb.	.06¾
Cobalt oxide, bbls.....lb.	2.10	Salicylate, cases.....lb.	.42	Bisulfite, bbls.....lb.	.04
Cod-liver oil, bbls.....bbl.	41.00	Methyl chloride, cylinders.....lb.	.55	Bromide, bbls.....lb.	.42
Collodion, drums.....lb.	.23	Michler's ketone, bbls.....lb.	3.00	Carbonate, sal soda, bbls., 100 lbs.	1.30
Copperas, c/l., bulk.....ton	13.00	Monoethylaniline, drums.....lb.	1.05	Chlorate, kegs.....lb.	.06¾
Copper, metal, elec.....100 lb.	12.90	Naphtha, solvent, tanks.....gal.	.35	Chloride, bags.....ton	12.00
Copper carbonate, bbls.....lb.	.16½	Naphthalene, flake, bbls.....lb.	.05	Cyanide, cases.....lb.	.20
Chloride, bbls.....lb.	.28	Nickel, metal.....lb.	.35	Fluoride, bbls.....lb.	.08¾
Cyanide, drums.....lb.	.48	Nickel salt, single, bbls.....lb.	.10½	Metallic, drums, 12¼-lb. bricks, lb.	.27
Oxide, red, bbls.....lb.	.16½	Double, bbls.....lb.	.09	Naphthionate, bbls.....lb.	.55
Sulfate, c/l., bbls.....100 lb.	5.05	Niter cake, bulk.....ton	4.50	Nitrate, crude, bags, N. Y. ....100 lbs.	2.45
Cotton, soluble, bbls.....lb.	.40	Nitrobenzene, drums.....lb.	.10½	Nitrite, bbls.....lb.	.08
Cream tartar, bbls.....lb.	.26	Oil, castor, No. 1.....lb.	.14	Perborate, bbls.....lb.	.21
Cyanamide, bulk, N. Y. ....Ammon. unit	1.67½	China wood, bbls.....lb.	.15½	Peroxide, cases.....lb.	.27
Diaminophenol, kegs.....lb.	3.80	Coconut, Ceylon, tanks.....lb.	.08½	Phosphate, trisod.....lb.	.04
Dianisidine, kegs.....lb.	2.85	Cod, N. F., tanks.....gal.	.62	Picramate, kegs.....lb.	.69
Dibutyl phthalate, drums, wks.....lb.	.29½	Corn, crude, tanks, mills.....lb.	.09½	Prussiate, bbls.....lb.	.12
Diethylaniline, drums.....lb.	.55	Cottonseed, crude, tanks.....lb.	.08¾	Silicate, drums, tanks, 40°, 100 lbs.	.75
Diethylene glycol, l. c. l. lots, drums.....lb.	.20	Lard, edible, bbls.....lb.	.15¾	Silicofluoride, bbls.....lb.	.04¾
Carload lots, drums.....lb.	.15	Linseed, bbls.....lb.	.096	Stannate, drums.....lb.	.48½
Diethylphthalate, drums.....lb.	.24	Menhaden, crude, tanks.....gal.	.46	Sulfate, anhyd., bbls.....lb.	.02¾
Diethylsulfate, tech., drums.....lb.	.20	Neat's-foot, pure, bbls.....lb.	.16½	Sulfide, cryst., bbls.....lb.	.02¾
Dimethylaniline, drums.....lb.	.30	Oleo, No. 1, bbls.....lb.	.17½	Solid, 60%.....lb.	.03½
Dimethylsulfate, drums.....lb.	.45	Olive oil, denat., bbls.....gal.	1.25	Sulfocyanide, bbls.....lb.	.40
Dinitrobenzene, drums.....lb.	.15½	Foots, bbls.....lb.	.09¾	Thiosulfate, reg., crys., bbls.....lb.	.02½
Dinitrochlorobenzene, bbls.....lb.	.15	Palm, Lagos, casks.....lb.	.08	Tungstate, kegs.....lb.	.80
Dinitronaphthalene, bbls.....lb.	.32	Peanut, crude, tanks.....lb.	.12	Strontium carbonate, bbls.....lb.	.08
Dinitrophenol, bbls.....lb.	.31	Perilla, bbls.....lb.	.13	Nitrate, bbls.....lb.	.08¾
Diphenylamine, bbls.....lb.	.45	Rapeseed, bbls., English.....gal.	.87	Strychnine alkaloid, 100 oz., powd.....oz.	.56
Diphenylguanidine, bbls.....lb.	.68	Red, bbls.....lb.	.09¾	Sulfate, powder.....oz.	.38
Epsom salt, tech., bbls., c/l., N. Y.....100 lbs.	1.10	Soy bean, crude, bbls.....lb.	.09¾	Sulfur, bulk, mines, wks.....ton	19.00
Ether, nitrous, bot.....lb.	.90	Sperm, 38°, bbls.....gal.	.84	Sulfur chloride, red, drums.....lb.	.05¾
Ether, U. S. P., drums.....lb.	.15	Whale, bbls., natural winter.....gal.	.76	Yellow, drums.....lb.	.03¾
Ethyl acetate, 85%, drums.....gal.	.85	Ortho-aminophenol, kegs.....lb.	2.20	Sulfur dioxide, commercial, cyl. ....lb.	.08¾
Bromide, drums.....lb.	.50	Ortho-anisidine, drums.....lb.	2.35	Sulfonyl chloride, drums.....lb.	.10
Chloride, drums.....lb.	.22	Ortho-dichlorobenzene, drums.....lb.	.06	Thiocarbonyl, bbls.....lb.	.22
Methyl ketone, drums.....lb.	.30	Ortho-nitrochlorobenzene, drums.....lb.	.32	Tin, Amer., stand.....lb.	.58
Ethyl benzyl aniline, 300-lb. drs. ....lb.	1.05	Ortho-nitrophenol, bbls.....lb.	.85	Tin bichloride, 50% sol., bbls.....lb.	17¾
Ethylene dichloride, tanks.....lb.	.06	Ortho-nitrotoluene, drums.....lb.	.17	Oxide, bbls.....lb.	.75
Chlorohydrin, anhyd., drums.....lb.	.75	Ortho-toluidine, bbls.....lb.	.29	Titanium oxide, bbls., wks.....lb.	.40
Glycol, c/l., wks.....lb.	.30	Palladium, metal.....oz.	80.00	Toluene, tanks.....gal.	.35
Ethyl ether, drums, cars.....gal.	1.79	Para-aminophenol, kegs.....lb.	1.15	Tribromophenol, cases.....lb.	1.10
Feldspar, bulk.....ton	20.00	Para-dichlorobenzene.....lb.	.17	Triphenylguanidine, drums.....lb.	.69
Ferric chloride, tech., bbls.....lb.	.07½	Paraldehyde, tech., drums.....lb.	.26	Triphenyl phosphite, bbls.....lb.	.75
Ferrous chloride, cryst., bbls.....lb.	.05	Para-formaldehyde, cases.....lb.	.45	Tungsten.....WO unit	10.50
Ferrous sulfide, bbls.....100 lbs.	2.50	Para-nitroaniline, drums.....lb.	.48	Urea, pure, cases.....lb.	.18
Fluorspar, 95%, bags.....ton	25.00	Para-nitrochlorobenzene, drums.....lb.	.32	Whiting, bags.....ton	18.00
Formaldehyde, bbls.....lb.	.09	.....lb.	.32	Xylene, 5°, drums, mills.....gal.	.35
Formaniline, drums.....lb.	.38	Para-nitrophenol, bbls.....lb.	.50	Xylidine, drums.....lb.	.37
Fuller's earth, bags, c/l., mines.....ton	15.00	Para-nitrosodimethylaniline, bbls.....lb.	.92	Zinc, metal, N. Y.....100 lbs.	6.40
Furfural, 500-lb. drs., c/l.....lb.	.17½	.....lb.	.30	Zinc ammonium chloride, bbls.....lb.	.05½
Glauber's salt, bbls.....100 lbs.	1.00	Para-nitrotoluene, bbls.....lb.	.30	Chloride, granulated, drums.....lb.	.06¾
Glucose, 70°, bags, dry.....100 lbs.	3.14	Para-phenylenediamine, bbls.....lb.	1.15	Oxide, Amer., bbls.....lb.	.07¾
Glycerol, C. P., drums.....lb.	.21	Para-toluidine, bbls.....lb.	.40	Stearate, bbls.....lb.	.19
				Zinc dust, bbls., kegs, c/l.....lb.	.09