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The Priestley Medal

Among the honors bestowed in America for attainments in the field of science, the Priestley Medal of the American Chemical Society is unique. It is the only medal in the gift of the national Society. It was founded to perpetuate the memory of an unusual investigator who began his work in England and completed it at Northumberland, Pa., where he became a man of importance. The name of Priestley is significant in chemistry, for it is associated with the discovery of oxygen. It is of particular importance to American chemists, since the birth of the American Chemical Society may be traced to the gathering at Northumberland in 1874 of a group of chemists who came to mark especially the centenary of Priestley's discovery of oxygen. The first American Chemical Society meeting was held April 6, 1876, in New York.

The medal was established through the efforts of Professor Phillips, of the University of Pittsburgh, who died before he saw his work completed, and of the late Edgar Fahs Smith, who did more than any other individual to determine the many interesting details of Priestley's life and work and record them in the permanent literature. Fully recognizing that our science advances not alone through the work of those who specialize in it, we award the medal for "distinguished services to chemistry."

That it is held in highest esteem by American chemists will be noted from the fact that it is bestowed triennially, and but two impressions have been struck. The first was presented to Ira Remsen in 1923, and the second to Edgar F. Smith in 1926. At the Columbus meeting the Priestley Medal Committee unanimously voted to award the third impression of the medal to Francis Patrick Garvan. Upon official notification that he was to receive this unique honor, Mr. Garvan wrote the Secretary of the Society as follows:

> My dear Mr. Parsons:
>
> I beg to acknowledge your letter of May 4th and to thank you and the American Chemical Society for the great honor they have conferred upon me in awarding the Priestley Medal for the services I have been privileged to render for the advancement of chemical knowledge and chemical education in this country. It is with great pleasure that I accept this signal mark of your Society's approval of the work I have been privileged to do for our common cause.
>
> Yours very truly,
>
> Francis P. Garvan

When the completion of work in progress makes possible the release of further data, so the story can be really told, it will be found that to Mr. Garvan has been given the extraordinary privilege of advancing chemistry in America in a way that is without parallel. He came to the science trained and prominent as an attorney. He was first interested when, in the Department of Justice and in the office of the Alien Property Custodian, he obtained a close insight into the influence of chemistry upon the everyday affairs of every man. His activity first became known to chemists through the Chemical Foundation, that great unselfish institution which has stood sometimes quite alone in the front rank of those who would see assured to America a complete chemical industry founded upon research of the highest order.

Surely the history of the Chemical Foundation is well known to our readers. The Society has stood by the Foundation through its various legal battles, from which it emerged completely triumphant and designated in court decisions as an organization approaching the relations of a trustee in regard to the protection of the American chemical industry and an aid to its continued progress. It may not be generally known that, in litigation in self-defense, and in meeting the many attacks of persecution, the Foundation has exhausted its resources from time to time and its needs have been met from private funds. Throughout, it has adhered to the ideals laid down by its president, Mr. Garvan, and has constantly supported, with its own funds and private funds given in its name and further funds given personally by Mr. and Mrs. Garvan, the advancement of chemical knowledge among the laity, the furtherance of chemical education, and the support of fundamental research. Let us list briefly some of the high spots in this remarkable record.

For seven years the *Journal of Physical Chemistry* has been made possible by the financial support of the Chemical Foundation. Following the high peak of publication costs in 1920 and 1921, when the Directors found it necessary to take $20,000 from invested money to maintain our publication program, this amount was restored to our capital from the funds of the Foundation. The special anniversary number of the *Journal of the American Chemical Society*, issued on the occasion of our Fiftieth Anniversary, was also made possible by such funds, and following the large Philadelphia meeting Industrial and Engineering Chemistry was enabled to print, without undue delay, many of the special papers because the Foundation provided a sum of $5000 for this purpose. The *Journal of Chemical Education*, which has risen rapidly from a small beginning to a publication serving in a special way some ten thousand subscribers, has been financed, and the business management assumed, by the Chemical Foundation. *Chemical Abstracts* has benefited largely from Foundation support, and at the present time $50,000 annually is being paid into the fund which is to be the nucleus of endowment to assist in maintaining, with a satisfactory degree of completeness, this key to the chemical literature of the world. When it was found that, to make the most of the data that have been assembled in the preparation of International Critical Tables, volumes beyond those originally planned should be published and further funds would be required to edit these volumes, the Chemical Foundation was one of those who generously supported the continuation of that valuable work at a time when the trustees scarcely knew where to turn for additional financing.

But perhaps our readers who are familiar with these important facts may fail to appreciate what has been done in connection with the Prize Essay Contest, now in its seventh year. Our many members who have served on committees to further contests within the states and to judge papers know something of what is involved, but even they cannot realize the great amount of effort and large funds that have been necessary to organize and conduct this work. The prizes themselves and the organization necessary to conduct the work involve an expenditure of about $50,000 annually, and this is met from the private fortune of Mr. and Mrs. Garvan. To collect and perfect lists of science teachers in the country has cost a substantial sum, much travel has been involved, printing bills have been large, and correspondence has required expert attention and a considerable volume of work. Seventeen thousand high and preparatory schools have been presented with 85,000 books, and many hundreds in addition have been given as prizes for the best papers in schools, as well as with honorable mention in state contests. Through books prepared for use in the contest, a tremendous impression has been made upon important men and women in the country with respect to chemistry and the need for its support. The two volumes of "Chemistry in Industry" and the companion volume of "Chemistry in Agriculture" have been distributed to the extent of 50,000 copies each. The latest in the series, "Chemistry in Medicine," is now in its second hundred thousand, while 250,000 sets of books familiar to our readers have been distributed. The pamphlet, "What Price Progress?," was demanded in excess of 600,000 copies and, in addition to all this, other literature of educational character has been distributed. An extensive use of these books has been made in interesting and obtaining support for education and for research. Several universities, in seeking large endowments which have been found, have used these volumes most successfully. Such results from a Prize Essay Contest in high and preparatory schools, and later extended to the college freshmen and to those preparing to teach would ordinarily not be expected. And yet, but for this contest, it is doubtful whether this useful literature would have come into existence. Certainly it would not have been made so generally available.

The Prize Essay Contest has always been of much interest to the daily press, and upon the announcement of the 1929–30 contest the *New York Times* commented editorially. The theme of the editorial was the contrast between the efforts being made by the Chemical Foundation and the AMERICAN CHEMICAL SOCIETY, working together to inform the people of the United States concerning scientific progress and what it means to them, and conditions which obtained but a few years ago in Russia. An American traveling there met a teacher of chemistry in a technical school who said that his people did not know what had been going on in the scientific world for the preceding four years, and added specifically that he did not know what Langmuir had been doing in Schenectady. Set over against this state of things, which happily has since been somewhat repaired, the statement that in the last Prize Essay Contest more than fifty thousand students submitted essays on subjects within the field of chemistry, based on information that had been made immediately available from the laboratories in every part of the country! What had been beyond the reach of even trained scientists in Russia because of political conditions at that time is brought to the very doors of the youth of America, and through them to their elders. The Prize Essay Contest, the editorial continues to point out, seeks to promote no private interest or enterprise, but only to help the oncoming generation to appreciate what this particular science is making available.

When the poet and philosopher Lucretius two thousand years ago urged men to study the atom ("considera opera atomorum") he was doubtless not thinking of the practical value, except as it might give the human spirit greater freedom. It was an intellectual consideration. The following of the achievements of the chemist should lead the minds of men out into wider horizons, quite apart from what it will do to lay the foundations for further practical achievements.

One important group of patents administered by the Chemical Foundation has to do with Imhoff tanks. The royalties have been devoted to research in sewage disposal, a field which had been practically neglected up to that time. With this beginning, the Foundation financed a conference of those particularly interested. Out of this meeting has grown the Federation of Sewage Works Associations with its quarterly "Sewage Works Journal," which already has a circulation of more than twelve hundred, and affords a special vehicle for the dissemination of research in sewage furthered and financed by the Foundation, as is the journal. At the University of Illinois fundamental research on sewage is in progress. This is a part of the sewage research also being conducted in New Jersey at the Agricultural Experiment Station, at the A. & M. College of Texas, at Iowa State College, and Penn State.

The first Institue of Chemistry of the AMERICAN CHEMICAL SOCIETY was made possible because the Foundation came forward to underwrite the deficit to the extent of $5000.

The standardization of biological stains was work financed entirely by the Foundation, and has enabled the stain manufacturers of America to sell their stains throughout the world. With this beginning, research under John W. Churchman at Johns Hopkins, looking to the use of stains as a vehicle in the treatment of diseases and malignant growths, has arisen. This, in turn, has made necessary further fundamental work on stains, leading to coördination and coöperation with those who are endeavoring to ascertain whether stains may not be useful in combating cancer. A specialist on this work is placed at the disposal of the Color Laboratory of the United States Department of Agriculture by the Foundation. In the James Buchanan Brady Urological Institute the work of Hugh Young is supported by the Foundation, and under the direction of John J. Abel the highly complex and baffling problem of the common cold is being attacked, aided by a grant of $195,000 for five years, to which, on account of progress made, $15,000 was added the second year. It required a deal of investigation before it was found that the medical fraternity considered the common cold problem so difficult that they hesitated to undertake to study it. But we may expect some valuable results, though perhaps not the ultimate answer to the problem, from the coöperative research now in progress at Johns Hopkins.

Chemomedical research at the Medical College of Virginia has been supported for three years, and for seven years the researches of Doctor Douchez on respiratory diseases have been furthered at Columbia University. We have a right to expect great things from the chemomedical research at the new medical center in New York City, where H. T. Clarke, so well known to our organic chemists, is assisting in the teaching of physicians and at the same time carrying on research. At the University of Illinois research in organic chemistry and high-pressure research receive Foundation support.

A considerable list? There is still a great deal to be added. Mr. and Mrs. Garvan personally have provided $60,000 by which Doctor Bloodgood, of Johns Hopkins, is conducting cancer research and the relation of dyes thereto, and have also established the chair of chemical education at Johns Hopkins, where already 17 four-year fellowships have been attracted from other individuals. Candidates are selected by states for research and study, and not necessarily with teaching as their objective. A man for research has been provided who also checks for accuracy articles that are submitted for publication in the *Journal of Chemical Education*.

And this is not all, for in supporting such work as here noted, Mr. Garvan and the Chemical Foundation have been able to interest others in similar causes. This has resulted now in the support of a productive individual that his work may go forward with greater rapidity; now in the provision of equipment needed in some laboratory; and again in providing generous endowment or whole new laboratory plants. If one could but bring together all of the bona fide instances of students supported because of the Prize Essay Contest, all students of ability who have chosen chemistry as a career, and all the culture added in homes as a result of the books distributed, it would make a total quite beyond ordinary measure.

It is evident that Mr. Garvan did not take up chemistry as a mere fad. He has seen in it potentialities that, if known to its devotees, were not explained to the nontechnically trained. He has seen visions and dreamed dreams, and has been in position to make some of these dreams come true.

Small wonder that in casting about for the third recipient of the Priestley Medal the committee found no one more entitled to this, the highest honor which the national SOCIETY can bestow for "distinguished services to chemistry."

The award will be the outstanding event at Minneapolis.

Reagents in Industry

NOW that our readers have had ample opportunity to familiarize themselves with the information contained in our July issue, we wish to emphasize the importance of two of the accomplishments reported therein.

Some one has said that one of the numerous methods for measuring the civilization of a country is by its production and consumption of sulfuric acid, and chemical technologists require no figures to convince them of the importance of this basic reagent. Notwithstanding the introduction of the contact process, chamber plants have continued to be installed and improved, and from time to time we have published discussions relative thereto. These have included new methods for the introduction of oxides of nitrogen. Certain strengths of acid have been produced in the lead chambers at a price lower than was possible by the contact process until the newer types of catalysts were devised. It is predicted that, with the latest type of contact mass which so successfully resists poisoning and which is said to effect such a satisfactory percentage of conversion, at last lead chambers are to be superseded, since the acid can be produced cheaply enough to permit dilution and still show a substantial saving over chamber acid. To reduce the cost of such an important industrial reagent as sulfuric acid should mean much for the chemical industry.

In many a laboratory the long list of Friedel and Crafts syntheses, worked out and described some fifty years ago, will now be reinvestigated from the standpoint of commercial utility, since at last aluminum chloride is available in carload lots. This reagent has been in use for years in substantial quantities for the manufacture of high-grade gasoline from high-boiling petroleum oils and has found further application in the refining of lubricating oils. The more extended use of this reagent was delayed, pending patent litigation which was but recently settled in the Supreme Court. Fortunately, this obstacle has been removed and aluminum chloride becomes an industrial chemical available at prices much lower than was ever anticipated. Perhaps still greater demand may make possible production on an even larger scale with consequent savings and, in turn, new avenues of utilization.

Those who make fundamental reagents available to industry at a cost permitting more extensive use perform services the beneficial effects of which will be felt for many a year to come.

By Their Fruits

IN THE printed record of the hearings before the Senate Finance Committee considering the Tariff Act of 1929, there appears, beginning at page 150, the testimony of a man who, in stating whom he represented, skilfully failed to indicate his real interest and those for whom he actually spoke. He gave as his principals, organizations with American addresses, but left it to the American manufacturers and the Synthetic Organic Chemical Manufacturers Association of the United States to inform the committee that he really appeared on behalf of the I. G. and its controlled American plants. The purpose of his appearance was to argue the desirability of greatly reducing tariff rates, and he undertook to show that the American industry, which he does not represent, no longer needs the assistance which only a proper tariff can give.

According to his testimony, our domestic dyestuff industry now supplies 97.8 per cent by poundage and 92.8 per cent by value of the domestic consumption of dyes of the class and kind which are manufactured in the United States. Disregarding some of the pertinent facts in the situation, he argued that American valuation on dyestuffs is cumbersome and no longer necessary, and that the multiple specific duty system should be eliminated. He made no mention of the fact that, under the present tariff, which was the method adopted by the United States to insure an American coal-tar industry, our domestic manufacturers have made highly creditable progress in both variety and quantity of dyes produced and with prices continually declining, nor that competition has been severe among domestic producers, with dye consumers reaping the benefit. He particularly avoided reference to the work which still lies before us, especially with respect to vat dyes, in the development and production of which protection similar to that which is now enjoyed is imperative. The charge is made that the present tariff plan is unsatisfactory in its operation. The witness overlooked that it has been in effect for six and one-half years, that according to his own testimony it affects but 25 per cent of the dyes imported, and that under it imports have inincreased until about 20 per cent of our consumption by value is now imported. The totals for the first six months of 1928 were 2,699,464 pounds, valued at $2,145,410. Corresponding figures for the same period of 1929 are 3,267,478 pounds, worth $2,627,558.

In other words, as was to be expected, it was the biased testimony of one identified with the importing interests and with foreign manufacturers and not one who has at heart the welfare of the American industry and all that that means to the American people. Surely the committees in Congress will not be misled by such testimony.

But to us the important point in all this is that it offers further evidence of what may be expected from the American I. G. The prospectus issued by the National City Company undertook to show that the American I. G. was being organized to develop the American industry. Here we have evidence that the disruption of the American chemical industry is what is sought, if that can be accomplished through taking from that industry such protection as the tariff affords it. Its representative has appeared before the Senate Finance Committee and, relying upon his previous connection with the United States customs laboratory as evidence of his expertness, urges substantial lowering of tariff rates. Frankly, we had hoped for evidences of better faith on the part of the new organization.

STEARIC ACID SYMPOSIUM

Papers presented before the meeting of the New York Group of the Division of Rubber Chemistry of the American Chemical Society on March 20, 1929

Adsorption of Stearic Acid by Carbon

J. T. Blake

Simplex Wire & Cable Co., Boston, Mass.

IN A PREVIOUS paper (*1*) a new theory of pigment reënforcement was presented in which a reënforcing filler was defined as one which forms a bond with the rubber matrix that is stronger than the matrix itself. At the same time the mechanism of filler dispersion was discussed and it is the purpose of this paper to amplify that discussion.

It is well known that there are certain materials occurring naturally in raw rubber or that may be deliberately added, such as stearic acid, which are responsible for the satisfactory dispersion of fillers. Harkins' ideas on dispersions may be applied to the situation.

Plantation rubber contains approximately 2 per cent fatty acids, chiefly stearic. These fatty acids are polar compounds containing a long hydrocarbon chain and an end carboxyl group. According to Harkins this sort of material is an excellent dispersing agent. When such a dispersing agent is used in rubber, the carboxyl group is attached to the surface of the filler particle and the hydrocarbon chain is dissolved in the rubber hydrocarbon. This covers the surface of the filler particle with a monomolecular film of the dispersing agent, each molecule being rigidly oriented. The result of such an action is twofold: it separates each particle from the others by the rubber matrix and causes the matrix to adhere firmly to the surface of the filler.

By taking into account the size of the filler particles and the molecules of the dispersing agent, it is possible to calculate the amount of material required to disperse a given quantity of filler in rubber.

The dispersion of carbon black in rubber is usually incomplete when more than 30 volumes are incorporated in 100 volumes of rubber. The amount of stearic acid necessary to produce a perfect dispersion of that amount of filler is calculated to be 1.95 per cent on the rubber. There is approximately 2.2 per cent naturally occurring fatty acids in the rubber, a very good agreement with the theory.

If this is the mechanism of the dispersion, certain deductions may be made. When carbon black or any other filler is dispersed in rubber, the fatty acid is adsorbed on the filler surface; in other words, the filler is wet by the acid and not the rubber hydrocarbon. The change in heat content when a filler is mixed into rubber should therefore be the heat of wetting of the filler by fatty acid and not by the rubber hydrocarbon.

The heat of wetting of carbon by fatty acid has been found by Gaudechon (*2*) to be 6.0 calories per gram of carbon. Hock (*3*) has found the heat of wetting of carbon black by rubber to be 5.1 calories per gram of carbon at 30 volumes carbon per 100 volumes of rubber. The agreement between these figures is satisfactory, but it is desirable to check this value by an independent method.

Determination of Cohering Voltages

The determination of cohering voltages has recently attracted attention as a new method of studying adsorption. The cohering voltage of a material is the voltage required to remove an adsorbed film of it from a surface.

This cohering voltage is measured in a coherer, which consists of a glass bulb containing two touching electrodes. The electrodes may be of tungsten, platinum, or carbon. They are glowed out in a high vacuum to remove all previously adsorbed material. The material whose cohering voltage is to be measured is admitted and allowed to become adsorbed on the surface of the filament electrodes. If a low voltage is applied to them, they are found to be completely insulated from each other by the adsorbed film. A definite voltage is applied to the film by charging a condenser to this voltage from a potentiometer and connecting it to the electrodes. The junction is then tested for conductivity by means of the very low voltage of a heated thermocouple in series with a galvanometer. If increasing voltages are successively applied to the electrodes, a definite voltage is found at which the junction ceases to be an insulator and is electrically conducting. The film of material has been desorbed from the electrode surface. The applied voltage has swept off the adsorbed molecules. This critical voltage is the cohering voltage and has a definite value for each adsorbed material. It varies from a small fraction of a volt to 10 or 12 volts. Non-polar hydrocarbons, such as pentane, have very low values (0.4 volt), while water, which is a strongly polar molecule, has a value of 11 volts.

Calculation of Energy Relations of Heat of Desorption

This voltage is thus a measure of the force of adsorption of the film involved. The exact mechanism of the desorption is not known, but the energy relations may be calculated closely. If the size of the molecules in the adsorbed film, the dielectric constant of the material, etc., are known, it becomes possible to calculate the heat of desorption. This value is of course equal and opposite in sign to the heat of adsorption.

The total heat of desorption of one mol of a substance is

$$Hm = \frac{AE^2(K - 1) \times 16}{d} + L$$

where Hm = heat of desorption of one mol
A = area occupied on the surface by one mol in square centimeters multiplied by 10^{16}
E = critical or cohering voltage
K = dielectric constant of material in adsorbed film
L = molar latent heat of evaporation of material of film
d = half thickness of the film

For an oriented film the film thickness is the length of the molecule. Since in an homologous series adsorption occurs with the same chemical group, the ratio between E^2 and the length of the molecule in carbon atoms should be a constant. Palmer (*5*) has recently measured the value of this ratio for a series of fatty acids and finds it to be 4.2. For a series of alcohols the value is 4.4, implying that the adsorption is quite similar. It would seem that the active group in a fatty acid is the hydroxyl as in an alcohol. From the above relation stearic acid should have a cohering voltage of 8.9 volts, since it has an equivalent length of 19 carbon atoms.

The molar heat of vaporization may be estimated quite accurately for stearic acid at 13,930 calories by Trouton's rule. Its dielectric constant was measured in this laboratory at 1000 cycles at 25° C. and found to be 2.27. The values of A and d are given by Langmuir (*4*) as 22 and 12.5 square Ångström and Ångström units, respectively. From these values the total heat of desorption which equals the heat of adsorption is calculated to be 64.5 calories per gram of stearic acid. Using this value, it may be calculated that if rubber contains 2.2 per cent fatty acids and 30 volumes of carbon black may be successfully dispersed in 100 volumes, the heat of wetting of the carbon black by stearic acid is 4.7 calories per gram of carbon. Thus the heat of dispersion as calculated from cohering voltages checks Hock's experimental value of 5.1 calories and in turn is checked by Gaudechon's value of 6.0 calories for the wetting of carbon by acid. Additional evidence is thus given that the heat of wetting of carbon by rubber is the heat of adsorption of fatty acids by carbon. The agents that disperse carbon black in rubber are the naturally occurring fatty acids, principally stearic.

Conclusion

The equations used in the calculations are based on the assumption that the adsorbed molecules are dipoles and are adsorbed in an oriented condition. That the values check is evidence that the proposed theory of dispersion is correct and that the dispersing agent is in an oriented condition on the surface of the filler particle. It is possible to calculate that the center of the dipole axis is 4.2 Ångströms from the filler surface. Since this value is but 20 per cent of the length of the stearic acid molecule, the carboxyl group is the chief contributor to its dipole moment. This would imply that the length of the hydrocarbon chain is probably not critical so far as the dispersing properties of a fatty acid are concerned.

The mechanism of the successful dispersion of fillers other than carbon black should be essentially the same. The whole theory throws much light on the essential part that the naturally occurring fatty acids and added stearic acid play in the dispersion of carbon black in rubber and explains why the addition of small amounts of stearic acid to rubber, especially to rubbers deficient in the naturally occurring dispersing agents, tends to produce a better and more uniform product.

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(2) Gaudechon, *Compt. rend.*, **157**, 209 (1913).
(3) Hock, *India Rubber J.*, **74**, 454 (1927).
(4) Langmuir, *J. Am. Chem. Soc.*, **39**, 1848 (1917).
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Discussion

C. R. Boggs

Doctor Blake has suggested a theory for the mechanism of filler dispersion and reënforcement. However, he deals only with carbon black in rubber. Carbon black is the most important reënforcing ingredient we have for a tire-tread compound. Being a conductor, it cannot be used in appreciable quantities in insulation. We might consider the possibility of finding a non-conducting reënforcing filler for insulation and also what should be done when the present supply of natural gas is depleted. What is needed is a material similar to clay which is cheap and has a small particle size. With present dispersing agents, clay does not, however, reënforce rubber to anywhere near the extent that carbon black does.

For a filler to reënforce satisfactorily it must be well dispersed and adhere firmly to the rubber. The correct dispersing agent should bring this about. This agent should be a polar compound. One portion of the molecule should be soluble in the rubber hydrocarbon and another portion should be capable of being adsorbed by and adhering strongly to the surface of the clay.

It would be laborious to mix clay in rubber with every material that might fulfil the above requirements for a dispersing agent and then test the product. What is needed is a relatively quick laboratory method of testing that will parallel the action of the filler in rubber. Two methods suggest themselves. The first one is that of determining the cohering voltages of various polar compounds on a clay surface. Unfortunately, clay is a non-conductor and is not adapted to use as electrodes in a coherer. The second method would consist of making a stiff paste of the filler with kerosene. The addition of a small amount of a suitable dispersing agent would thin the paste to a mobile liquid. Kerosene, being a long-chain hydrocarbon, should resemble rubber as a dispersing medium and the experiment should be analogous to the dispersion of the filler in rubber.

We have made a number of mixes of clay and kerosene and added various dispersing agents. Seventy-five per cent nitrobenzene by weight on the clay did not produce a satisfactory dispersion. Although the nitrobenzene is a strongly polar compound, no part of the molecule is apparently adsorbed by the clay. Twenty-two per cent stearic acid did produce a good dispersion, while only 2 per cent wool grease was required to reduce the stiff paste to a thin liquid. These results indicate that a small quantity of wool grease would transform clay to a strong reënforcing filler in a rubber compound. Rubber-clay compounds containing 2 per cent wool grease on the filler were mixed and cured. Their physical properties were not appreciably different from the same compounds without the wool grease. In other words, the kerosene experiment is not parallel to conditions in the rubber compound.

Present laboratory methods for examining dispersing agents are inadequate for the development of new ones and improving the ones we have now. New methods should produce materials that would do the same thing for other fillers that stearic acid does for carbon black. More theoretical work on adsorption and dispersion should develop new reënforcing fillers and be of great benefit to the rubber industry as a whole and the wire trade in particular.

Nature, Manufacture, and General Use of Stearic Acid

D. F. Cranor

Binney & Smith Co., 41 East 42nd St., New York, N. Y.

Stearic acid is a colorless, waxlike material, melting at 69.3° C. and having a specific gravity of 0.847 at this temperature. It belongs to the saturated series of fatty acids of the type indicated empirically by the formula $C_nH_{2n}O_2$, being the member having 18 carbon and 36 hydrogen atoms, and is probably best written $CH_3(CH_2)16$-COOH.

Occurrence

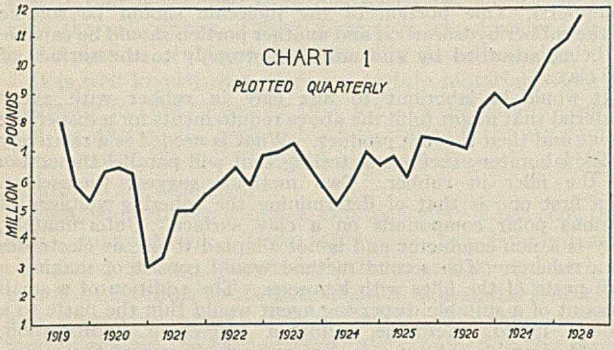
Stearic acid occurs in nature as the triglyceride principally in the solid animal fats commonly called tallows, and, in fact, derives its name from the Greek word meaning tallow. It is associated with the glyceride of oleic acid, which is the member of the unsaturated class containing the same number of carbon atoms, and to a lesser extent with palmitic acid, which stands immediately below stearic in the saturated series. In the article of commerce stearic acid very largely predominates, but it follows from its natural occurrence that appreciable amounts of oleic and some palmitic acid are also present in proportions which vary somewhat according to the grade.

Grading

The gradings are designated according to method of manufacture—namely, as single-, double-, and triple-pressed stearic acid. As will be shown, the product is purified by various degrees of pressure, which removes increasing amounts of the liquid oleic acid and, broadly speaking, these grades represent the following composition:

GRADE	STEARIC ACID	OLEIC ACID
	Per cent	*Per cent*
Single-pressed	85	15
Double-pressed	90	10
Triple-pressed	95	5

The terms "saponified" and "distilled," which obviously are also derived from processes involved in manufacture, have through usage become designations accepted as indicating differences which are of some importance to certain consumers—as, for example, the manufacturers of candles, crayons, and cosmetics. It will, however, be apparent to the chemist that all stearic acid is saponified; and distillation, when employed, is a subsequent operation separate and distinct from saponification.



SALES OF STEARIC ACID — TEN YEAR PERIOD

Commercial Raw Material

Tallow is the material extracted from the solid fat or suet of cattle, sheep, hogs, and horses. The quality varies with the season, the food and age of the animal, and the method of rendering, but always consists chiefly of stearin and olein. High-grade tallows and the similar material, yellow grease stearin, are the principal raw materials employed in the manufacture of the so-called saponified grade. The natural color of this product is a light amber, and since very particular users, such as crayon manufacturers and certain others, prefer saponified acid on account of its harder texture and slightly lower content of palmitic acid, and have come to associate brownish color with good quality, usually no attempt is made to decolorize this grade. Slaughterhouse grease, garbage grease, and similar materials of darker color are the raw materials for the production of the distilled grade, these being rendered usable through the purification effected by the distillation process. It so happens that the cost of this processing very nearly equals the savings effected through the utilization of cheaper materials, and it is a matter of efficiency and economy of resources for the manufacturer to equip for the preparation of both grades. Distilled acid is usually of somewhat lighter color than saponified material of equal melting point and similar oleic acid content, but it is not naturally colorless and the snowwhite products are obtained by resort to special decolorizing methods.

Processing

Saponification is accomplished through use of the Twitchell or similar type of reagent. In some cases cooking in an autoclave under steam pressure is used.

Naturally the process of manufacture in different plants varies as to detail. The following description briefly outlines the procedure of one modernized plant, the essentials of which are generally applicable to the industry as a whole.

The first operation is a washing, carried out in large wooden tanks equipped with open steam coils. Crude grease is run in, dilute sulfuric acid added, and the mixture is cooked with live steam for approximately $1^1/_2$ hours. The principal purpose of this operation is the removal of mechanical impurities.

The charge is then run to another steam tank, where saponification is carried out. The Twitchell reagent is added here and the stock boiled for 18 to 20 hours, at the end of which time the sweet water (glycerol) obtained as a by-product is run off.

A so-called second boil follows, and the crude fatty acid stock, free from glycerol, is again cooked in the tank employed for the original saponification. This treatment raises the fatty acid content to around 97 to 98 per cent. If the grade of grease employed is such as requires distillation in addition, the fatty acid mixture from the second boil is transferred to the distilling department; but if the saponified grade is being prepared, the charge is sent direct to the storage tanks in the cold-press department. For distillation a typical fatty acid still is used, which is copper-lined and operated with superheated steam under vacuum. The distillate is a highly refined fatty acid mixture, running a little less than 50 per cent stearic acid, and the residue in the still is the material known as stearin pitch.

The crude fatty acid in the melted state is piped into pans and allowed to cool and solidify. The cakes thus formed are wrapped in cloth and pressed in a large hydraulic cold press somewhat similar to those used in the rubber industry. This first pressing requires about $2^1/_2$ hours and produces a material of lower grade than any used in rubber compounding. Further removal of oleic acid is required; and this is accomplished by pressure under elevated temperature conditions.

The cold-pressed acid is melted and again cascaded into pans and formed into cakes, which are wrapped in coarse cloth in preparation for hot-pressing. The conditions of the operation govern the grade of the final product.

Triple-pressed stearic acid is subjected to two hot presses—the first for 3 to $3^1/_2$ minutes, and the second for 5 to 6 minutes with steam of 120 pounds pressure continuously circulating through the press. Double-pressed acid receives one hot pressing, which is of relatively long duration. Single-pressed acid of the standard rubber grade is also hot-pressed, and differs from the double in that the period of hot-pressing is shorter—namely, 3 minutes instead of 5. The time intervals mentioned above are the actual pressing periods and do not include the time consumed in loading and bringing up the press, the over-all time being considerably longer.

Each grade is melted and boiled with sulfuric acid in a large tank in order to improve the color. The product is drained while hot and is finally drawn off through pipes and again cascaded into pans which serve as molds to form slabs of finished product.

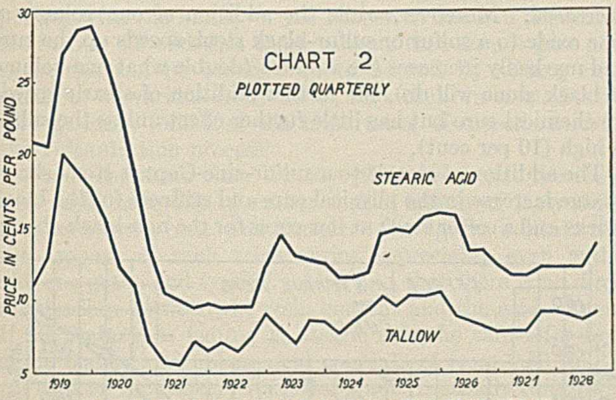
Requirements for Rubber

There are two important factors which determine the suitability of stearic acid for rubber compounding—namely, the proportion of oleic acid and the total fatty acid content. The requirements for rubber are therefore covered when the specifications imposed regulate (1) melting point or titer, (2) iodine absorption value (Hanus number), and (3) percentage of free fatty acid.

As is sometimes the case when a new raw material is taken up by the rubber industry, an unnecessarily high quality of stearic acid (usually the double-pressed distilled grade) was first employed. The price of fatty acids was relatively low during the years of the principal development of its use in rubber, and to be sure of obtaining a satisfactory quality the candle-makers' material, a white, bleached product, was very generally adopted. Since that time, and particularly with the wider use of stearic acid as an important activator of certain organic accelerators, a closer study of the essential properties has been made. The rubber compounder now realizes that color is not to be regarded among quality criteria, and although it is quite generally understood that the blooming tendency is principally due to the oleic acid component, compounding and processing means have been devised to minimize this condition and the rubber industry has standardized on the undecolorized single-pressed grade. Grades lower than standard single-pressed have been avoided for rubber because higher proportions of oleic acid are detrimental to the aging of certain types of rubber compounds.

Commercial Position

The value of stearic acid as a rubber ingredient is so generally recognized that the rate of production and the price trend are now matters of considerable interest to the compounder. (Chart 1) During the war period plant facilities were increased to meet the heavy demand created by the then existing conditions. However, the industry encountered a severe depression during the period of readjustment and, even upon recovering, ran through the years from 1923 to 1926 on a low level, averaging around 25 million pounds per year against a capacity approximating 100 million. Since the last half of 1926 there has been steady, continuous growth in production and sales, which is explained by the wider use of candles for decorative purposes and the increased use in rubber. In 1928 the total production of stearic acid, including all grades, ran close to 41 million pounds; but it is seen from the foregoing that, even with this increased production, only about 40 per cent of the capacity of the industry is employed; and, since the rubber use accounts for only 30 per cent of the total, it will be apparent that the 12 million pounds used in rubber during 1928 can be greatly increased without taxing the manufacturers' resources.



PRICE OF STEARIC ACID AND TALLOW— TEN YEAR PERIOD
DOUBLE PRESSED GRADE

Price

The price curve of stearic acid has followed, and run approximately parallel to, the cost of tallow, and frequently has deviated from the direction of the sales curve. The direct relation between the price of stearic acid and the tallow market is illustrated by Chart 2, showing the record of these two commodities during the past decade. This picture also indicates the moderateness of the current prices.

As a matter of fact, fatty acid manufacture consumes only from 15 to 16 per cent of all the grease produced; practically all of the rest goes to the soap industry. Thus, it is seen that the price of stearic acid is governed by conditions which are current in industries entirely beyond the control of the producer of fatty acid.

Stearic acid has a definite chemical function in rubber compounding; but although the rubber chemist thoroughly appreciates this fact, he all too frequently thinks of stearic acid as one of the softeners. The specific gravity of the commercial product is 0.85. This is, without exception, the lowest figure to be found in a table of some seventy compounding ingredients and brings the volume cost of the standard rubber grade to 13.2 cents a pound volume, based on the current carload price of 15.5 cents per pound. Occasionally one hears it remarked that stearic acid is a rather high-priced softener, whereas it really should not be regarded as a softener at all. Actually, it is used to improve cheap rubbers, to stabilize the cure of the better grades, or to activate an accelerator; and the improved workability which also results may be justly regarded as an extra advantage obtained through the use of this ingredient. Not much, if any, less stearic acid would be consumed by the rubber industry if it effected no softening action, and when employed to act in the role of a softener or dispersing agent it is invariably selected because there is no other substance available to accomplish the improvement which it imparts through its function in the vulcanization reaction.

When added to brown plantation crepe rubbers, or other offish sorts, for the purpose of enhancing the quality of the vulcanizate, a less expensive and better product results through the presence of the stearic acid, and usually no appreciable amount of cheap softener is displaced. In tread compounds and similar types it assists in dispersing the reënforcing pigment and incidentally facilitates factory processing, but is used primarily for its own setting-up effect, and accomplishes this at a cost of the same order as that of the pigment employed. Priced today at a figure which is but a slight fraction more than one-half the cost of crude rubber, stearic acid would have to advance to more than 27 cents per pound to equal the volume cost of rubber when the pound price of that commodity is 25.

Production of Coal-Tar Crudes

The Tariff Commission has issued the following table showing the production and value of coal-tar crudes in 1928 by firms not primarily engaged in the operation of coke-oven plants and gas houses:

NAME OF PRODUCT	PRODUCTION	VALUE
Carbolic oil or middle oil (gallons)	200,899	$ 26,455
Dead or creosote oil (gallons)	134,460,126[a]	17,507,588
Naphthalene, crude (pounds)	46,157,425[b]	531,752
Other distillates (gallons)	6,709,519	1,005,972
Pitch of tar (tons)	514,902[c]	8,425,461
Refined tars (barrels)	1,640,282	7,543,457
Solvent naphtha (gallons)	6,676,656[d]	1,437,518

[a] Includes 12,386,000 gallons of dead oil produced in by-product coke plants.

[b] Includes 12,182,143 pounds of crude and refined, produced in by-product coke plants.

[c] Does not include 54,131 tons produced in by-product coke plants.

[d] Includes 5,587,370 gallons of solvent naphtha produced in by-product coke plants.

Stearic and Oleic Acids as Rubber-Compounding Ingredients

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It is proposed in this brief discussion to touch upon the relative effects of stearic and oleic acids in a few typical rubber stocks; then to discuss certain anomalies as to the effect of stearic acid on chemical and physical cure; and, lastly, to consider some of the differences found by use of different accelerators.

Inasmuch as oleic acid is the chief impurity in commercial stearic—running from 10 to 15 per cent—it seems desirable to know the behavior of oleic acid alone.

Comparison of Stearic and Oleic Acids

The following data show the comparative effects of double-pressed stearic and commercial oleic acids in typical rubber compounds:[1]

Table I—Action of Stearic and Oleic Acids in Typical Rubber Compounds

Captax Tread—4 parts acid on 100 rubber
23 volumes black
1 volume ZnO
Best cure, 70 minutes at 127° C. (260° F.)

	Stearic	Oleic
Cure at 127° C., minutes	70–100	70–100
Modulus at 300 per cent, kg. per sq. cm.	68–90	61–75
Acid bloom after 15 hours[a]	None	Very bad

Captax Friction—0.6 part acid on 100 rubber
$\frac{1}{2}$ volume ZnO
8 parts softener
Best cure, 40 minutes at 127° C.

	Stearic	Oleic
Cure at 127° C., minutes	40–50	40–50
Modulus at 700 per cent, kg. per sq. cm.	85–97	78–85
Acid bloom[a]	None	No bloom, but very sticky

Zinc Oxide Friction—2 parts acid on 100 rubber
$7\frac{1}{2}$ volumes ZnO
$4\frac{1}{2}$ parts softener
Best cure, 30 minutes at 127° C.

	Stearic	Oleic
Cure at 127° C., minutes	30–40	30–40
Modulus at 300 per cent, kg. per sq. cm.	63–78	53–68
Acid bloom[a]	None	No bloom, but more tacky than control

[a] Uncured stock.

From these data it would appear that, in Captax stocks, there is a distinct loss in modulus due to the substitution of stearic acid by oleic. This seems to be more pronounced in the loaded stocks. From the point of view of acid bloom, the tread stock was the only one giving trouble, but this is serious. It would thus appear that purified stearic acid might be desirable for carbon black stocks, whereas for friction stocks, where modulus is not always so important, less pure stearic could be used, particularly if additional tack is desired. It must be borne in mind that these conclusions are, so far, limited to Captax.

Behavior of Stearic Acid

Let us now turn to stearic acid itself. We will note a few things about its behavior with zinc oxide and carbon black. It is necessary to distinguish between the effect on physical and chemical cure. This is shown by some unpublished work by C. R. Park, a summary of which is given in Tables II and III.

Bracketed ingredients denote original materials in the rubber mix (except rubber). Material appended to bracket by plus sign is that which gives the effect on cure noted in the adjoining columns. Physical cure picked by hand. Vol. = volume loading on 100 volumes rubber; blk = micronex carbon black; acid = stearic acid; stiff. = modulus as shown by stress-strain curve.

Table II—Effect of Stearic Acid on Physical and Chemical Cure

Composition	Combined Sulfur	Physical Cure	Stiff.
[25 vol. blk. + 8 pts. S] + 4 acid	Same	Same	Less
[25 vol. blk. + 8 pts. S] + $3\frac{3}{4}$ vol. ZnO	Inc. 70%	Inc. 15%	Inc. 70%
[25 vol. blk. + 8 pts. S + $3\frac{3}{4}$ vol. ZnO] + 4 acid	Inc. 15%	Inc. 15%	Inc. 3%
[20 vol. blk. + 3 pts. S + 1 vol. ZnO + 1.2 Captax] + 4 acid	Dec. 8%	Inc. 50%	Inc. 40%
[6 pts. S] + 1 vol. ZnO	Same	Inc. 16%	Inc. 40%
[3 pts. S + 1 vol. ZnO + 1.2 Captax] + 4 acid	Curves cross	Dec. 20%[a]	Curves cross
[10 pts. S] + 1 vol. ZnO		10% faster	Inc. 50%
[10 pts. S] + 4 acid		20% slower	50% less
[10 pts. S + 1 vol. ZnO] + 4 acid		Same	30% Inc.
[$3\frac{1}{2}$ pts. S + 1 vol. ZnO] + 4 acid		Slight Inc.	Slight Dec.
[$3\frac{1}{2}$ pts. S + 1 vol. ZnO + 4 acid] + 0.5 Captax		Cures $\frac{1}{10}$ time	Great Inc.
[6 S] + 1 vol. ZnO		Inc. 10%	Inc. 100%
[6 S + 1 vol. ZnO] + 4 acid		Dec. 10%	Inc. 20%
[6 S + 1 vol. ZnO + 4 acid] + 0.25 Captax		Inc. 90%	Inc. 600%

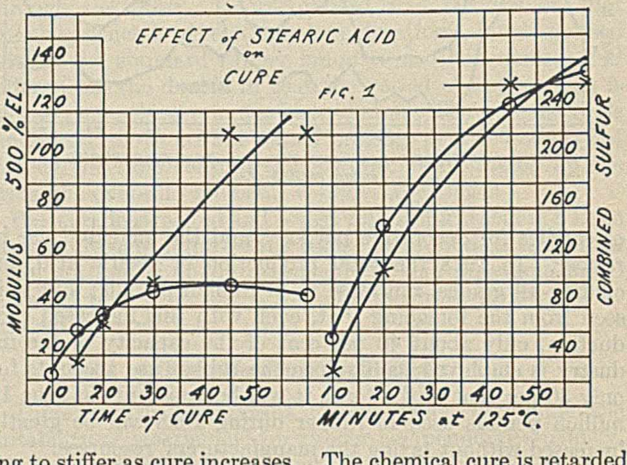
[a] See Figure 1.

Table III—Comparison of Stiffening Effect of Zinc Oxide and Black

	(Kg./cm.^{2}) @ 700%
6 S + 1 vol. ZnO	52
6 S + 1 vol. Micronex	25
6 S + 1 vol. Thermatomic	26

Here we see that if stearic acid is added to a sulfur mix there is a marked decrease in chemical and physical cure. In a sulfur-black stock the cure is unchanged but the stiffness is decreased. Moreover, while the addition of one volume of zinc oxide to a sulfur or sulfur-black stock speeds up the cure and markedly increases the stiffness (double what one volume of black alone will do), the further addition of stearic speeds up chemical cure but has little further effect unless the sulfur is high (10 per cent).

The addition of stearic to a sulfur-zinc-Captax stock shows a large increase in the physical cure and stiffness for the black stocks and a softer stock at low cures for the non-black changing to stiffer as cure increases. The chemical cure is retarded in both cases.



Hence it would seem that stearic acid is, by itself, a retarder of chemical and physical cure. With zinc oxide it changes to an accelerator of chemical cure and with Captax to an accelerator of physical cure. Here, however, even in the presence of zinc, the chemical cure is retarded.

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[1] This work was done by R. W. Beveridge of the compounding staff of the Goodyear Tire & Rubber Co.

Action of Other Accelerators

The writer has previously published (*1*) a so-called accelerator classification which considered various typical groups of accelerators. The following remarks will apply to these groups only:

Work with extracted rubber shows: (1) All accelerators are improved by zinc oxide; (2) the zinc oxide must be rendered rubber-soluble by stearic acid except in the case of the dithiocarbamates and the thiurams which are capable of reacting directly with zinc oxide; (3) Captax and derivatives must have zinc in soluble form to function at all; (4) P-nitroso will function in extracted rubber in the absence of zinc oxide but, if zinc oxide is present, it must have stearic also. Hence it would seem that the prime function of stearic acid is to furnish zinc oxide in a suitable form for the use of the accelerator. Otherwise it acts as a softener and retarder. As to why an excess of stearic acid retards diphenylguanidine and has no such action on other accelerators, it is hard to say. Perhaps there is a more or less stable diphenylguanidine stearate formed which is a non-accelerator. Certainly there is much to be explained as to the mechanism of the zinc soap in the physical cure of rubber.

Literature Cited

(1) Dinsmore and Vogt, *Trans. Inst. Rubber Ind.*, **4**, 85 (June, 1928); *Rubber Age*, **23**, 554 (1928).

Effect of Stearic Acid on Various Crude Rubbers

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DURING the last few years considerable work has been done in determining the effect of increasing amounts of stearic acid in various types of compounds using different accelerators. The work described herein emphasizes the point that in comparisons of this kind a third variable may enter—namely, the crude rubber—and if fine distinctions are to be drawn as to the correct amount of stearic acid to use with any particular accelerator some consideration should be given to possible variations in the rubbers used.

Russell (*1*) shows that when different crude rubbers are cured with zinc oxide certain samples give compounds with very poor physical properties while other samples give good results. He connects the tendency to give well-cured compounds with the ability of the rubber to dissolve zinc oxide. He further showed that those rubbers that do not give good properties can be brought up to normal by adding small amounts of various fatty acids, and thus, in a qualitative way at least, indicated the importance of organic acids to the vulcanization process.

About the same time Whitby (*2*) showed that the resins that occur naturally in rubber consist largely of fatty acids, such as stearic, oleic, and linoleic. His figures indicate that the amount of such acids varies appreciably even within any one grade and type of rubber and that there is no direct relationship between the resin content and the acid content. If all the acid is figured as stearic acid, he shows for first-grade plantation rubbers acid contents of from 0.50 to 1.92 per cent on the rubber; for lower grades it usually runs lower. He gives a mean value of 1.35 per cent acid for plantation grades and further states that types of rubber other than Hevea usually contain little or no free acid.

In later work Whitby and his co-workers (*3*, *4*) study the effect of adding increasing amounts of organic acid to rubber that has been extracted with acetone until it is practically resin-acid free and then compounded with several type accelerators. They show a varying effect with different accelerators and also indicate that the effect may be appreciable when organic acids are added even within the normal acid range for Hevea rubber samples. A summary of the previous work that has been done by other investigators on the influence of fatty acids on vulcanization is also given by Whitby and Evans (*3*).

Experimental Procedure

Various grades of rubber were selected in order to obtain a range of acid values. Each grade was blended on a mill to obtain uniformity and then an average sample taken for the acid determination. For this purpose 30 grams were extracted with acetone and the extract was then titrated with alcoholic potash. Instead of using Whitby's designation "acid number" (milligrams of KOH to neutralize the acid from 100 grams of rubber), all results have been figured as though the resin acids were entirely stearic acid and the acid content is then given as per cent stearic acid on the rubber.

Results

Some of the results obtained by using these rubbers of known acid value in several type formulas are given below. The results have been compressed to show tendencies in as few comparisons as possible rather than to give actual detailed results, as the purpose of this paper is to indicate a condition and no attempt has been made to cover the whole ground of possible variations.

Table I—100 Rubber, 10 Sulfur

Cure at 50 lbs. (3.2 kg. per sq. cm.) steam pressure (148° C.)	90 Minutes		105 Minutes		120 Minutes	
Tensile in lbs. per sq. in. (kg. per sq. cm.)	Break	800% Elong.	Break	800% Elong.	Break	800% Elong.
	SMOKED SHEET—1.36% RESIN ACID					
Control	2050 (144.1)	1100 (77.3)	2350 (165.2)	1400 (98.4)	2450 (172.3)	1650 (116.0)
+ 1% Stearic acid	1950 (137.1)	1000 (70.3)	2250 (158.2)	1325 (93.2)	2400 (168.7)	1600 (112.5)
	AMBERS—0.79% RESIN ACID					
Control	2200 (154.7)	1300 (91.9)	2400 (168.7)	1800 (126.5)	2600 (182.8)	2100 (147.6)
+ 1% Stearic acid	2150 (151.2)	1250 (87.9)	2350 (165.2)	1700 (119.5)	2600 (182.8)	2050 (144.1)
	ROLL BROWN—0.20% RESIN ACID					
Control	1350 (94.9)	750 (52.7)	1650 (116.0)	1000 (70.3)	1800 (126.5)	1250 (87.9)
+ 1% Stearic acid	1300 (91.9)	700 (49.2)	1575 (110.7)	900 (63.3)	1750 (123.0)	1200 (84.4)
	CAUCHO BALL—0.12% RESIN ACID					
Control	1050 (73.8)	500 (35.1)	1150 (80.8)	750 (52.7)	1350 (94.9)	900 (63.3)
+ 1% Stearic acid	1000 (70.3)	500 (35.1)	1200 (84.4)	650 (45.7)	1350 (94.9)	850 (59.7)

RUBBER-SULFUR—Table I shows four rubbers of varying acid content used in the simple formula 100 rubber and 10 sulfur. Each stock was cured with and without 1 per cent of added stearic acid. The tensiles and moduli are shown for three cures of each set. It is noted that in this type formula the addition of 1 per cent stearic acid had very little effect on either tensiles or moduli, although, if anything, there is a slight tendency to lower both.

RUBBER–SULFUR–ZINC OXIDE–DIPHENYLGUANIDINE—Table II gives three rubbers in a diphenylguanidine formula both with and without the addition of 1 per cent stearic acid. In this case the high resin-acid rubber (smoked sheet) shows a very noticeable drop in physical properties when 1 per cent stearic acid is added, while the other two rubbers are practically unaffected. The total acid in the case of the smoked sheet becomes appreciable after the 1 per cent stearic is added (2.36 per cent on the rubber).

Table II—100 Rubber, 6 Zinc Oxide, 3.5 Sulfur, 1 Diphenylguanidine

Cure at 35 lbs. (25 kg. per sq. cm.) steam pressure (138.5° C.)	30 Minutes		40 Minutes		50 Minutes	
Tensile in lbs. per sq. in. (kg. per sq. cm.)	Break	600% Elong.	Break	600% Elong.	Break	600% Elong.
SMOKED SHEET—1.36% RESIN ACID						
Control	2800 (196.8)	1600 (112.5)	3050 (214.4)	2150 (151.2)	3350 (235.5)	2600 (182.8)
+ 1% Stearic acid	2500 (175.8)	1300 (91.9)	2800 (196.8)	1550 (108.9)	3100 (217.9)	1800 (126.5)
EARTH SCRAP—0.20% RESIN ACID						
Control	2650 (186.3)	1100 (77.3)	2900 (203.9)	1350 (94.9)	3000 (210.9)	1500 (105.5)
+ 1% Stearic acid	2600 (182.8)	950 (66.8)	2850 (200.4)	1200 (84.4)	2950 (207.4)	1435 (103.7)
ROLL BROWN—0.20% RESIN ACID						
Control	2050 (144.1)	850 (59.7)	2350 (165.2)	1100 (77.3)	2450 (172.2)	1200 (84.4)
+ 1% Stearic acid	2000 (140.6)	800 (56.2)	2400 (168.7)	1050 (73.8)	2500 (175.8)	1200 (84.4)

RUBBER–SULFUR–ZINC OXIDE–HEPTENE—Table III covers the same comparison as the previous one except that an aldehyde-amine type of accelerator (heptene) is used in place of diphenylguanidine. Here again the high resin-acid smoked sheet shows a decrease in physical properties on the addition of stearic acid. But when the low resin-acid rubbers are considered, it is seen that the addition of stearic acid improves both the tensiles and moduli very appreciably and if anything the rubber with the lowest natural acid content shows the greatest improvement. The total acid in these three low acid rubbers is 1.12 to 1.2 per cent on the rubber.

Table III—100 Rubber, 6 Zinc Oxide, 3.5 Sulfur, 0.5 Heptene

Cure at 35 lbs. (2.5 kg. per sq. cm.) steam pressure (138° C.)	30 Minutes		40 Minutes		50 Minutes	
Tensile in lbs. per sq. in. (kg. per sq. cm.)	Break	600% Elong.	Break	600% Elong.	Break	600% Elong.
SMOKED SHEET—1.36% RESIN ACID						
Control	2700 (189.8)	1250 (87.9)	3100 (217.9)	1700 (119.5)	3150 (221.5)	1900 (133.6)
+ 1% Stearic acid	1800 (126.5)	750 (52.7)	2400 (168.7)	1050 (73.8)	2700 (189.8)	1500 (105.5)
EARTH SCRAP—0.20% RESIN ACID						
Control	1000 (70.3)	150 (10.5)	850 (59.7)	200 (14.0)	1000 (70.3)	250 (17.5)
+ 1% Stearic acid	1600 (112.5)	400 (28.1)	1850 (130.0)	500 (35.1)	2100 (147.6)	1050 (73.8)
ROLL BROWN—0.20% RESIN ACID						
Control	750 (52.7)	250 (17.5)	1050 (73.8)	350 (24.6)	1200 (84.4)	400 (28.1)
+ 1% Stearic acid	1850 (130.1)	575 (40.4)	2150 (151.2)	800 (56.2)	2400 (168.7)	900 (63.3)
CAUCHO BALL—0.12% RESIN ACID						
Control	800 (56.2)	250 (17.5)	1050 (73.8)	350 (24.6)	1200 (84.4)	400 (28.1)
+ 1% Stearic acid	1650 (116.0)	600 (42.2)	2150 (151.2)	800 (56.2)	2400 (168.7)	900 (63.3)

COMBINATION OF HIGH ACID AND LOW ACID RUBBERS—Table IV gives the heptene formula using (1) a high acid smoked sheet, (2) a mixture of 2 parts of high acid smoked sheet and 1 part low acid roll brown, (3) a mixture of the same two rubbers, but in the ratio 1 of smoked sheet to 2 of roll brown, and (4) the low acid roll brown alone. The total resin-acid values of the mixtures are also shown for each rubber combination. Here again there is a lowering of tensile and modulus when stearic acid is added to the high acid smoked sheet and a raising of these properties when this acid is added to the low acid roll brown. The two compounds containing the mixed rubbers show an increase of the physical properties roughly in proportion to the amount of low acid rubber present—i. e., to the lack of natural resin acids.

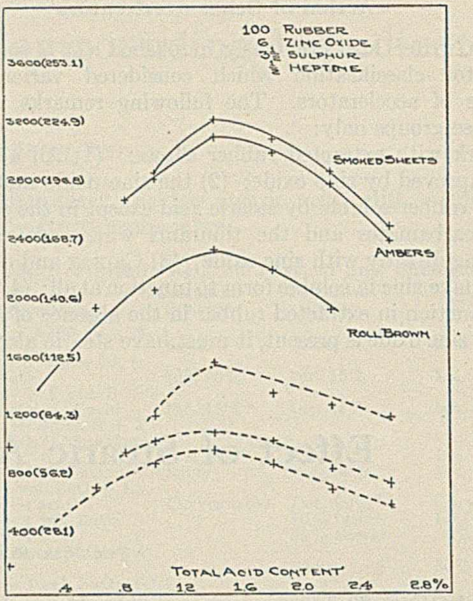

Figure 1

HEPTENE FORMULA WITH INCREASING AMOUNTS OF TOTAL ACID—In Figure 1 the heptene formula is shown using three different rubbers and increasing amounts of stearic acid so that the total stearic acid (resin acid plus added acid) varies from 0.2 to 2.6 per cent on the rubber. Stearic acid was added on the mill to give definite increases in total acid. Tensile and modulus at 600 per cent elongation curves are shown for a 40-minute cure at 35 pounds (2.5 kg. per sq. cm.) steam with three rubbers of varying amounts of resin

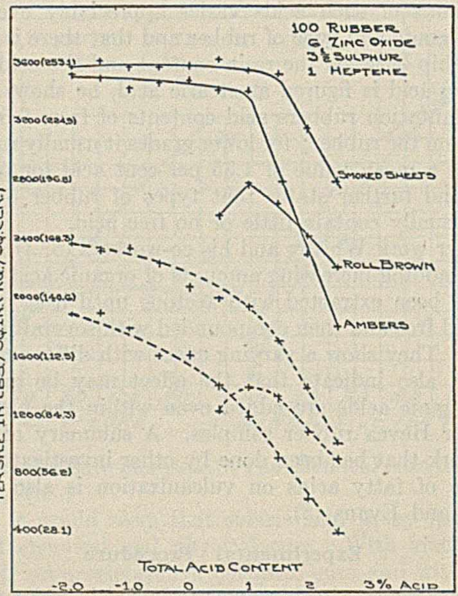

Figure 2

Table IV—100 Rubber, 6 Zinc Oxide, 3.5 Sulfur, 0.5 Heptene

Cure 40 minutes at 35 lbs. (2.5 kg. per sq. cm.) steam (138.5° C.)

	Smoked Sheet		2 Smoked Sheet 1 Roll Brown		1 Smoked Sheet 2 Roll Brown		Roll Brown	
Resin acid, per cent	1.36		0.97		0.88		0.20	
Tensile in lbs. per sq. in. (kg. per sq. cm.)	Break	600% Elong.	Break	600% Elong.	Break	600% Elong.	Break	600% Elong.
Control	3100 (217.9)	1700 (119.5)	1800 (126.5)	550 (38.7)	1400 (98.4)	400 (28.1)	400 (28.1)	200 (14.1)
+ 1% Stearic acid	2400 (168.7)	1050 (73.8)	2400 (168.7)	700 (49.2)	2200 (154.7)	650 (45.7)	1600 (112.5)	700 (49.2)

acid. The amount of resin acid present in each rubber is indicated by the first point at the left in the curve for the rubber. It is noted that in this formula all three rubbers show a quite definite maximum for both physical properties at a total acid content of approximately 1.4 per cent on the rubber, and that there is a falling off in tensile and modulus as the acid content varies on either side of this figure.

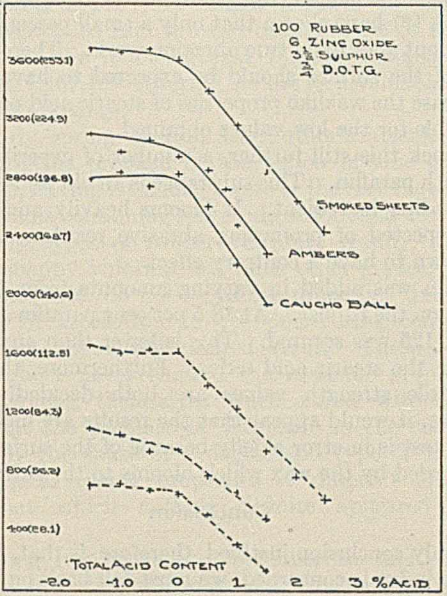

Figure 3

Heptene Formula Varying Total Acid from Plus to Minus—A heptene formula is shown in Figure 2 using three different rubbers and varying the amount of total acid (resin and added) between the limits −2.0 to +2.5 per cent on the rubber by adding on the mill the desired quantity of either stearic acid or alcoholic potash. The points shown are for equivalent states of cure; i. e., as alkali is added it is necessary to take a shorter time of cure to compensate for the accelerating effect of the alkali. In this case 1 per cent heptene is used in place of the 0.5 per cent used previously and this apparently tends to throw the acid maximum a little lower—nearer to 1 per cent acid. At approximately 1 per cent total acid there is a rather definite point of inflection on all the curves. Continued decrease of acid below this point does not cause a lowering of physical properties as was obtained in the previous figure, probably because the added alkali forms soap with the acid which tends to hold up the physical properties.

Di-*o*-Tolylguanidine Formula as Above—This comparison as given in Figure 3 covers the same ground as the one just shown except that di-*o*-tolylguanidine is used as the accelerator in place of heptene. In this case the point of flexing in all three curves appears to be close to zero acid content. There is very little change in physical properties as the acid content is increased above this.

Conclusions

The exact acid content of a compound has an important effect on the physical properties secured with it and there is probably a definite state of acidity for each accelerator, and perhaps compound, which gives the best results with the combinations in question.

The naturally occurring resin acids in rubber must be considered in figuring the total available acid in any compound. This is especially important where changes are made from one type or grade of rubber to another.

Acknowledgment

Acknowledgment is due to G. W. Cassell, formerly of The Fisk Rubber Company Research Laboratory, who conducted most of the experimental work covered in this paper.

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Effect of Increased Quantities of Stearic Acid on Tread Abrasions

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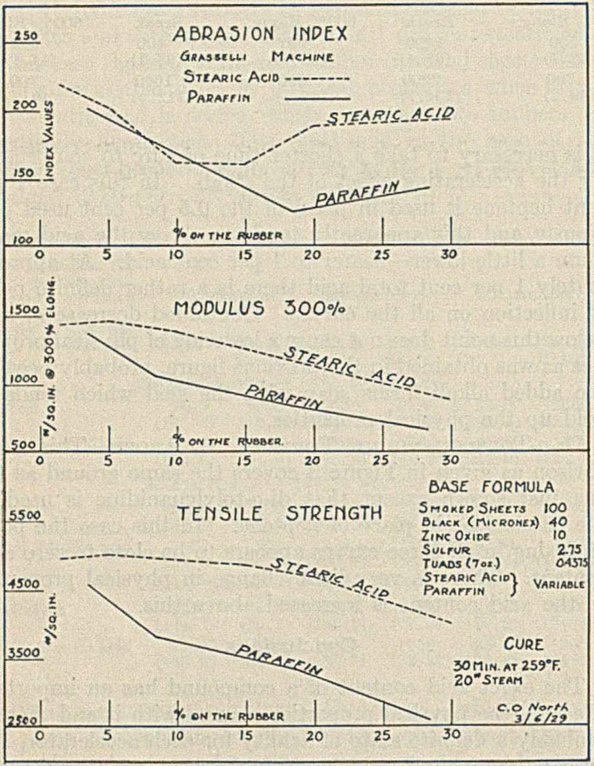
THE problem of laboratory abrasion tests on rubber which will allow one to predict something regarding the relative service of two tread compounds on the road is a very important one and has been attacked by many investigators.

Perhaps the best machine so far developed is the Grasselli abrader, invented by Williams (*3*) who states that "the Grasselli abrader is a machine for measuring the volume loss of rubber per unit of work expended. Its principle is similar to that of a Prony brake in which the rubber test pieces are similar to the friction surfaces of the brake." The abrasion index secured by the Williams method represents volume abraded, in cubic centimeters per horsepower-hour. The volume abraded is the volume loss of both test pieces and the horsepower-hour figures refer to full brake horsepower.

While the Grasselli abrader is perhaps the best abrasion machine now in existence, its results should not be taken as a final criterion. Williams states: "While the Grasselli abrader makes possible a real comparison of the abrasion resistance of any compound, it should not be expected to replace actual road tests." This sensible admonition has been disregarded by too many rubber technologists. The results obtained on this machine have been interpreted in ways not intended and conclusions have been drawn which are not correct.



It is well known that the introduction of certain higher fatty acids—e. g., stearic—into rubber compounds is beneficial. A deficiency is thus supplied and a uniformly vulcanizing compound is secured. Furthermore, stearic acid aids in the dispersion of pigments, such as carbon black. There is no question but that the moderate use of stearic acid in tread compounds is decidedly helpful.

However, there are people who believe that if a little is good, more is better. Stearic acid has been added as high as 9 per cent on the rubber. The resulting compounds gave, on the Grasselli abrader, index values much below what one would normally expect. It should be explained that the lower the index value—i. e., the less the volume loss per unit of power consumed—the better the tread, since the tire whose tread wears the longest is usually considered the most desirable.

Experimental

Any test which is applied beyond its reasonable limitations is dangerous. One simple method of attack is the "reduction to absurdity" procedure; this was followed.

A tread compound which vulcanizes nicely at low temperatures was selected (formula given on accompanying graph). Stearic acid was added in quantities from 1.5 to 30 per cent on the rubber. Batches were milled in the regular way and sheets and abrasion blocks vulcanized for 30 minutes at 126° C. (259° F.)(20 pounds steam). This cure was selected as previous work had shown it to be the optimum. Abrasion tests were made in accordance with the procedure recommended by Williams. Stress-strain curves were secured in the usual manner. The accompanying graph shows the variation in tensile strength, modulus (load necessary to produce 300 per cent elongation), and abrasive index with increased quantities of stearic acid.

It will be noted that the abrasive index falls until a minimum is reached at 10 per cent. This value is held until 15 per cent, when it begins to increase. It should also be noted that the value for 30 per cent stearic acid is less than that for 2 per cent, which is the normal quantity usually employed. In other words, if we are to believe the results, we should expect better tread wear, other things being equal, from the stock containing 30 per cent stearic acid than for the one containing 2 per cent.

The above did not appear to be a reasonable conclusion. The stocks from 3 per cent up, on examination were found to be rather heavily covered with stearic acid "bloom;" i. e., the stearic acid came to the surface and thus provided a lubricant, which interfered with the proper working of the test.

One's first thought on the subject would naturally be that lubrication of the surface should not materially affect the test because the index of abrasion represents volume abraded per horsepower-hour. But Plummer and Beaver (*1*) and also Vogt (*2*) have shown that only a small percentage of the power input goes to do true abrasion work. Therefore, lubrication of the surface should be expected to have an effect. In this case the waxlike properties of stearic acid probably are responsible for the low values obtained.

To check this still further, a number of experiments were made with paraffin. This substance is an old well-understood compounding ingredient. It blooms heavily and has never been suspected of promoting abrasive resistance. In fact, it is known to have a contrary effect.

Paraffin was added in varying amounts from 3.5 to 28.5 per cent on the rubber. At 18.5 per cent paraffin an abrasion index of 125 was secured. This is lower than any value obtained in the stearic acid series. Furthermore, the modulus and tensile strength values are both decidedly affected. Therefore, it would appear that the results are highly absurd and the test is in error chiefly because of the surface lubrication afforded by the wax which blooms to the surface.

Conclusion

The only conclusion justified, therefore, is that, in so far as abrasion index is concerned, we must fall back on road tests. There the values depend, not only upon the abrasion resistance of the tread, but also upon the design of the tire, its load, position on the car, etc. The Grasselli abrader is of value in laboratory work, but the results must always be carefully scrutinized and must be interpreted within the actual conditions of test.

Acknowledgment

The data contained in this paper were secured in the Akron laboratory of this company by Arnold H. Smith and C. O. Wheeler.

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Government Develops Method for Preparing Gas-Free Liquids

An improved method for removing and collecting dissolved gases from liquids has been developed by the Bureau of Standards. It has been found, for example, that under proper conditions, the amount of oxygen dissolved in water may be reduced to less than 0.0001 per cent by only one sublimation. Ammonia, carbon dioxide, and many other gases may be completely removed from liquids. This is of importance in accurately determining the vapor pressure, conductivity, and density of pure liquids.

It was discovered that, through the principle of vacuum sublimation, gas-free liquids could be prepared without appreciable loss of either liquid or dissolved gas. These liquids are used in the determination of physical constants.

Early Experiments with Stearic Acid in Rubber Compounding

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BEFORE 1921 stearic acid as an ingredient of rubber compounds was practically unknown. Most likely it was the widespread belief among rubber chemists that acidic substances should be avoided in rubber that kept the fatty acid so long in the background. At any rate, the author was unaware that any particular chemical value could be ascribed to acid substances in vulcanization until a series of investigations and discoveries forced him to the conclusion that stearic acid is a necessity for the poorer grades of rubber and by no means harmful to the best. These discoveries led him to make extensive use of the acid in 1921, and in the following year to apply for and obtain U. S. Patent 1,467,197 covering its use as a valuable ingredient of rubber mixings.

In the early spring of 1921 the author's attention was occupied with the problem of the action of zinc oxide in vulcanization, having been long aware of the fact that when a standard formula containing zinc oxide, sulfur, and accelerator is used many types of rubber vulcanize readily, yielding strong and snappy vulcanizates, while other grades, just as good in appearance, do not vulcanize properly. Increasing the amount of accelerator in the poor-curing compounds did not bring about the desired result. These varying grades of rubber never showed the same or proportional differences among themselves when cured without zinc oxide, so that the presence of the oxide in the compound was evidently the cause of a degree and type of variation in the technical curing properties of different grades of rubber, about which nothing definite appeared to be known.

The varying responsiveness of rubber to zinc oxide in vulcanization was in those days a great factory problem which necessitated the careful testing of all rubber shipments and as far as possible the blending of the bad rubber with the good in order to maintain some degree of uniformity in the finished product. In view of these manufacturing difficulties, the author was continually seeking an explanation of the extremely variable behavior of rubber and also for a practical means of overcoming it.

Effect of Resins on Zinc Oxide

While experimenting with plastic pitch and cumar resin, the remarkable observation was made that on curing a compound of rubber containing 3 per cent of zinc oxide, 5 per cent of resin, 6 per cent of sulfur, and some organic accelerator, the zinc oxide disappeared completely from the plastic pitch vulcanizates, which remained transparent, while when cumar was used the vulcanizates remained opaque and muddy brown. Both compounds, before curing, were white and opaque. After curing, 5 per cent of zinc oxide had gone completely into solution in the one, while in the other it had not.

Here obviously was a profound difference between these two resins with respect to their action on zinc oxide. It seemed reasonable to conclude that plastic pitch, being a pine resin and acid in character, had entered into chemical combination with zinc oxide and converted it into a rubber-soluble derivative, while cumar resin, being neutral, had produced no such chemical effect during vulcanization.

This consideration led to the suspicion that the phenomenon of the dissolution of zinc oxide in rubber might be closely related to that of the varying responsiveness of rubber to zinc oxide. To test this theory a sample of rubber known to be quite unresponsive to zinc oxide—in other words, a very poor curing type—was mixed with zinc oxide, sulfur, and accelerator and cured with the addition of 0.5, 1, and 2 per cent of plastic pitch, respectively. The surprising results obtained from this simple experiment were most illuminating and are given in Table I.

Table I—Effect of Plastic Pitch on Cure

Time of Cure at 148° C.	Control—No Pitch		0.5% Pitch		1% Pitch		2% Pitch	
	Tensile	Elong. at break	Tensile	Elong. at break	Tensile	Elong. at break	Tensile	Elong. at break
Min.	*Kg./cm.*^{2}	%	*Kg./cm.*^{2}	%	*Kg./cm.*^{2}	%	*Kg./cm.*^{2}	%
45	...	...	133.1	820	160.2	845	126.7	820
60	111.1	915	169.1	827	177.4	837	176.3	830
75	...	...	169.1	810	177.4	810	175.1	800
90	114.6	920	169.1	820	169.1	800	177.4	800
105	125.3	920	170.5	823	151.1	790	163.5	785
120	111.1	920	...	...	...	...	...	...

It was evident from the test figures and general appearance of the cures that small percentages of pine pitch exerted a profound and beneficial influence on the vulcanizing properties of the unresponsive rubber.

The effects of a variety of resins on the same lot of rubber were then examined and the results plainly showed that these resins could be classified into two groups according to their effect or lack of effect on the rubber under investigation. Resins that were found to improve the physical quality of the vulcanizate were plastic pitch, Venice turpentine, colophony, Burgundy pitch, and copal resin. These resins all had a very strong action. Resins which were found to have no action or only a slight one were dragon's blood, sandarac, elemi, mastic, guaiacum, dammar, and cumar.

Function of Acid in Vulcanization

The only explanation that could account for the profound difference in these two groups of resins was the fact that those in the first or active group were all acid substances, while those in the second or inactive group were neutral or practically so. It thus appeared probable that the presence of an organic acid was necessary for the proper technical vulcanization of rubber, and that the function of the acid must be to convert insoluble zinc oxide into a zinc salt or compound to some extent soluble in the rubber and consequently more likely to participate in chemical reactions during vulcanization.

To prove this theory the zinc salts of certain high-molecular-weight organic acids—namely, the resinate, stearate, and oleate—were substituted for the acid resin and were found to produce similar beneficial effects, particularly pronounced in the cases of the fatty zinc salts. The zinc salts were tested without free zinc oxide in the batch as well as with the usual amount of oxide, and it was found that their effect was far stronger in presence of free zinc oxide than when they were used alone.

It having been proved that zinc salts of organic acids such as stearic and oleic acids could produce the surprising effects originally obtained by means of acid resins, only to a greater degree, it was at once surmised that such acids themselves must be of great value in vulcanization.

These fatty acids were accordingly thoroughly tested in a great variety of samples of rubber, and in every case where the rubber by test showed a natural lack of response to zinc oxide it was found that the fatty acids corrected the defect and enabled the rubber to be vulcanized properly, yielding vulcanizates of greatly enhanced physical value. Table II gives some of the interesting figures obtained in the original series of experiments and shows the powerful action of stearic and oleic acids as well as that of pine pitch and zinc stearate in a very pronounced manner. The formula used was: rubber 100, zinc oxide 3, sulfur 5, and accelerator 0.15, and 2 per cent on the rubber of each of the above mentioned substances respectively was added.

Table II—Action of Acids, Pitch, and Zinc Stearate on Cure

TIME OF CURE AT 148° C.	CONTROL		2% PINE PITCH		2% STEARIC ACID		2% ZINC STEARATE		2% OLEIC ACID	
	Tensile	Elong. at break	Tensile	Elong. at break	Tensile	Elong. at break	Tensile	Elong. at break	Tensile	Elong. at break
Min.	*Kg./cm.*^{2}	%	*Kg./cm.*^{2}	%	*Kg./cm.*^{2}	%	*Kg./cm.*^{2}	%	*Kg./cm.*^{2}	%
45	81.4	903	140.4	890	173.6	845	171.4	853	167.7	867
60	89.4	910	178.7	880	182.4	827	187.1	810	198.4	817
75	99.8	923	179.1	837	189.7	810	191.2	787	190.1	797
90	112.5	920	202.9	850	181.4	793	165.8	760	175.5	780

The rubber used in these experiments was a plantation grade known as clean thin brown crepe, excellent in appearance and, as far as cleanliness was concerned, actually living up to its name. But vulcanization told a different tale and, as the results of the control test clearly showed, this particular parcel of plantation rubber was a very poor one. All its cures were soft and flabby, muddy brown in color, and possessed of a peculiar odor like that of burnt sugar. Doubling and even tripling the proportion of the accelerator had practically no effect. But the addition of 2 per cent of pine pitch, stearic acid, oleic acid, or zinc stearate changed the curing properties of the rubber entirely. The peculiar odor of the control was no longer perceptible, the muddy brown color cleared up, and the flabby weakness gave way to the strength and snappiness characteristic of the best curing rubber.

The tests were repeated with many samples of different grades of rubber. Some samples showed a very great improvement, others a less pronounced, and still others slight or no improvement, depending on the natural curing quality of the rubber. But all were brought up to substantially the same level of physical quality by the addition of the organic acid. Here, then, was a practical solution to the problem of the variable curing capacity of plantation and other rubber, as found in manufacturing practice, as well as a strong indication as to the cause of its strange variable behavior.

Most Effective Types of Acids

The results thus far obtained naturally raised the question as to what types of organic acids had the power of producing the remarkable results obtained from stearic and oleic acids. Attention was at first given the acids of the fatty series, and it was found that all available acids of the monobasic saturated fatty series, even including acetic acid (formic acid was not tested), had the power, more or less pronounced, of improving the cure of rubber naturally unresponsive to zinc oxide. The higher members, such as lauric, palmitic, and stearic acids, produced the most pronounced improvement, while the lower members of the series were much less active.

Many other organic acids were tried and it was found that such acids as benzoic, anisic, cinnamic, and phenylacetic also had a well-defined activity in promoting the vulcanization of unresponsive rubber. On the other hand, boric, oxalic, tartaric, salicylic, acetylsalicylic, β-oxynaphthoic, camphoric, and sebacic acids had no effect; in fact, some of these had the opposite effect and degraded the control.

Solubility of Zinc Salts in Xylene

At this stage of the investigation it became very desirable to know something about the solubility in rubber of the zinc salts of those acids which had proved themselves either active or inactive in rubber. Since, however, rubber did not lend itself to experiments of this sort with small quantities of materials, xylene was chosen as a solvent and small quantities of the zinc salts were heated in xylene at the boiling point and the rates of their dissolution studied. Thus it developed that the zinc salts of all those acids which had proved effective in rubber were more or less soluble in hot xylene, the salts of the most effective acids being the most soluble. In sharp contrast to this observation, the zinc salts of the acids which had no effect in rubber were found to be substantially insoluble in the hot hydrocarbon.

Solubility of Zinc Oxide in Xylene-Acid Solutions

The next question which suggested itself was this—Can a hot xylene solution of an acid which is active in rubber dissolve zinc oxide and if not, under what conditions can it be made to do so?

The method of investigation was simple and consisted in heating in 25 cc. of xylene containing a sufficiency of the dissolved acid, 0.05 gram—in other words, a mere pinch of zinc oxide, the disappearance or permanence of which, in the hot solution, could readily be observed. The results were interesting and instructive. With stearic acid (0.7 gram) there was no appreciable dissolution of the zinc oxide even on prolonged heating. The addition of a small quantity of urea (urea does not dissolve in the xylene, but remains in globules on the bottom of the vessel) caused the zinc oxide gradually to go into solution. Aniline had a similar but slower effect and had to be added in greater proportion. Pyridine readily brought about dissolution. Piperidine was found to be much more powerful in bringing the zinc oxide into solution than any of the other bases mentioned.

With benzoic acid (0.3 gram) there was again no dissolution of zinc oxide even on prolonged heating, but on the addition of piperidine complete solution was effected in a few minutes. Many other acids were subjected to the same test and the results in general seemed to demonstrate clearly that xylene solutions of organic acids which improve the vulcanization of rubber do not appreciably dissolve zinc oxide unless a basic substance is also present in the solution. By the same method it was shown that similar solutions of organic acids which are ineffective in rubber do not dissolve zinc oxide, even in the presence of organic bases.

It appeared that in order to be effective in rubber or able to dissolve zinc oxide in xylene solution, an acid must be monobasic. Dibasic acids failed to produce any beneficial effect in rubber and likewise failed to dissolve zinc oxide in xylene solution, even in presence of piperidine. Thus, while monobasic capric acid, $CH_3.(CH_2)_8.COOH$, is active, the corresponding dibasic sebacic acid, $COOH.(CH_2)_8.COOH$, is quite inactive. The former forms a xylene-soluble zinc salt; the zinc salt of the latter is insoluble even in presence of added bases.

Further investigations indicated that the influence of basic substances in facilitating the dissolution of zinc oxide in xylene solutions of organic acids is due to the formation of double salts. Many zinc salts found to be difficultly soluble in hot xylene became readily soluble on the addition of piperidine, pyridine, urea, ammonium carbonate, or even some aqueous ammonia. For instance, zinc benzoate was but slightly soluble, yet on adding a little pyridine it became readily soluble and the solution, on standing, deposited beautiful crystals of a salt which appeared to consist of 2 mols of zinc benzoate and 3 of pyridine. In a similar way double salts were obtained from zinc benzoate and ammonia as well as from zinc benzoate and hexamethylenetetramine.

These findings seemed to point to an intimate coöperation between the organic acid and the accelerator in bringing the zinc oxide into a soluble state in rubber mixtures during vulcanization. It is very probable that the nitrogenous accelerator is a necessary adjunct to the acid, and vice versa. Even in compounds containing no added accelerator the necessary conditions are no doubt fulfilled, since it is practically certain that ammonia and other active nitrogenous substances are formed from the rubber protein during vulcanization.

Experiments with Rubber Resins

The results of these investigations pointed to only one possible conclusion in regard to raw rubber and the type of variability under consideration—that rubber responsive to zinc oxide must contain naturally occurring organic acids capable of promoting the dissolution of zinc oxide in the rubber during vulcanization, while unresponsive rubber must lack such acids.

This assumption proved to be correct. Resin extracted from unresponsive brown crepe was found to be practically insoluble in cold dilute caustic potash, while that obtained from first-latex crepe (almost always highly responsive) dissolved easily, yielding a very soapy solution which, on shaking, formed an intense lather. The two opposite types of rubber resin were then dissolved separately in xylene and the solutions tested in the same way as were the organic acids previously described, and it was found that the resins from the unresponsive rubber had no power to dissolve zinc oxide even after the addition of piperidine and other bases, while under the same conditions the resin extracted from the responsive rubber dissolved zinc oxide with ease.

Study of Rubber Extract

Since it was thus proved that the acetone extract of first-latex rubber contained organic acids capable, in conjunction with bases, of promoting the dissolution of zinc oxide in xylene, which acids appeared to resemble the higher fatty acids in their general behavior, a chemical investigation of the extract was undertaken.

To this end a large quantity of first-latex rubber was extracted and yielded on an average about 2.26 per cent of extract. With the exception of small quantities of a white substance difficultly soluble in acetone and a crystalline sugar, the extract consisted of a thick brown oil, quite liquid when warm. On standing for several days, the oil became pasty and interspersed with nodules which under a microscope were seen to consist of fine silky needles. On spreading the pasty oil on a porous plate, most of the oily portion was absorbed, leaving the solid matter as a whitish paste. This paste was dissolved in warm alcohol from which solution silky white crystals separated. These showed a melting point of 65-67° C., which by repeated recrystallization from alcohol was raised to 69° C., the melting point of stearic acid. On mixing the purified substance with pure stearic acid the melting point remained unchanged, which fact, together with the absolute similarity in chemical behavior, proved that the solid constituent of the rubber oil was stearic acid.

Pure stearic acid was also obtained from crystals which proved to be potassium stearate, obtained by dissolving the rubber oil in caustic potash from which solution the crystals of potassium stearate had separated. The exact proportion of stearic acid in the oil was not determined, but it was estimated that it carried not less than 0.5 per cent of stearic acid calculated on the rubber.

Conclusions

1—Plantation rubber may be very variable in its reaction to zinc oxide on vulcanization and in this respect may be divided into three classes: (*a*) responsive to zinc oxide, (*b*) intermediately responsive, and (*c*) unresponsive.

2—Responsive rubber yields an extract which consists for the most part of organic acids, resembling in their chemical properties the higher fatty acids and actually containing a notable proportion of stearic acid. Unresponsive rubber yields an extract practically devoid of organic acids.

3—The organic acids in responsive rubber are the cause of the superior technical curing quality of the rubber, due to their power, in conjunction with basic substances or nitrogenous accelerators, of bringing zinc oxide into a state of solution in the rubber during the process of vulcanization. The lack of organic acids in unresponsive rubber is the cause of the imperfect curing properties of such rubber, for in this case the zinc oxide remains undissolved.

4—The addition of a fatty acid to unresponsive rubber corrects the defect in the rubber due to the absence of natural organic acids and puts the rubber on the same curing plane as responsive rubber, particularly when nitrogenous accelerators are used. It is thus possible, by adding a constant proportion of fatty acid to all rubber, to maintain a high degree of uniformity of cure for any given formula, irrespective of the natural variation of the raw rubber used.

Effect of Electricity on Corrosion

Although the electrolytic corrosion test method cannot be used as a simple routine test for determining the relative corrodibility of metals, it is a helpful method of studying corrosion phenomena in general, the Bureau of Standards finds.

It has corroded sheet copper and nickel in a solution of sodium chloride by applying a voltage to the electrolytic cell. In any particular test, both electrodes of the cell were made of the same metal, either copper or nickel.

The corrosive attack obtained when oxygen was used, either dissolved in the solution or used as the atmosphere surrounding the entire cell, was decidedly greater than when nitrogen was similarly used. The most interesting results, however, were obtained with partially submerged specimens, as compared with totally submerged ones, regardless of the other conditions obtained in the electrolytic test. The corrosive attack in the former case was very much greater.

This difference appears to be associated with non-uniformity in the distribution of oxygen or air. Those portions of the metal surface exposed to the solution with a slightly higher oxygen content set up a "galvanic" cell with those portions exposed to the solution where the oxygen content was lower.

This effect is independent of and in addition to the corrosive attack which the metal undergoes in the test "cell" as a result of an impressed voltage. The total loss obtained was greater than would be produced alone by the current resulting from the applied voltage. The general conclusions regarding the differential-aeration effect on corrosion are in general agreement with those of foreign investigators.

Effect of Stearic Acid on Reclaimed Rubber

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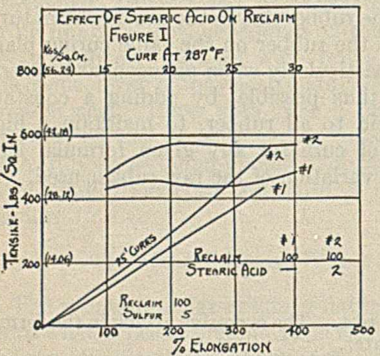
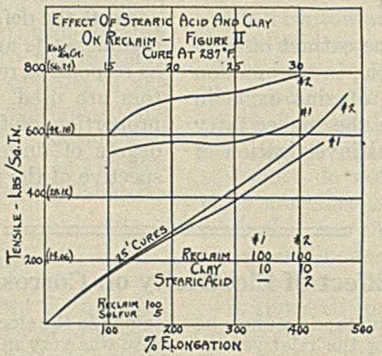
IT IS the purpose of this paper to discuss the effect of stearic acid on the process of manufacture of reclaimed rubber and its effect when used with reclaimed rubber in vulcanized rubber goods. The uses of stearic acid in reclaimed rubber can best be grouped as follows: (1) in the digester or heater as a plasticizing agent to speed up the disaggregation of the rubber; (2) when added to the plasticized rubber on the mill or in an internal mixer, to facilitate addition of a pigment or to impart some desirable property or consistency; (3) in compounds containing substantial amounts of reclaimed rubber.

In most reclaiming processes softeners are used in the devulcanizer in conjunction with heat, to aid in plasticizing the rubber. They may also be added on a warm-up mill or in an internal mixer to give a reclaim with desirable properties for tubing machine and calender operations. It may be desirable to have a definite amount or a complete absence of tack. It is therefore essential that the right softener is used and that it is added at the proper time. Factory conditions such as type of equipment, method, and speed of processing and cooling conditions determine the limits of firmness, softness, tackiness, plasticity, milling properties, and nerve of the reclaimed rubber required by the rubber goods manufacturer.

Effect of Softeners in Alkali Whole-Tire Reclaim

DIGESTER PROCESS—Table I shows some of the chemical and physical tests ordinarily run on samples of reclaim. Three experimental reclaims were prepared from the same lot of whole-tire scrap by the alkali process. In one case no oil was used for softening purposes, in the second 4 per cent of pine tar was added, and in the third 4 per cent stearic acid. The same amount of 6 per cent sodium hydroxide solution was used in each experiment. The samples were devulcanized 14 hours at 160 pounds (4.2 kg. per sq. cm.) steam pressure. As indicated by the comparative chloroform extracts and plasticity coefficients, the first reclaim was dry and harsh. It was very slow to break down on the mill and difficult to keep around the roll until broken down. The second reclaim using pine tar was much softer. Its consistency was about the same as that of an average high-grade whole-tire reclaim. The curing properties are improved. The third reclaim using stearic acid was also dry and harsh. On the mill it broke down slightly better than the reclaim containing no softener. The stearic acid is practically all converted to sodium stearate in the alkali process. This has no softening action and under these conditions has a drying action and removes all trace of "tack." This effect is obtained quite generally with the fatty acid soaps. In the alkali process of reclaiming, stearic acid does not have an opportunity of functioning as a softener because it is immediately converted to a soap. In the preparation of heater or digester reclaims in which no caustic soda is used, stearic acid functions as a softener.





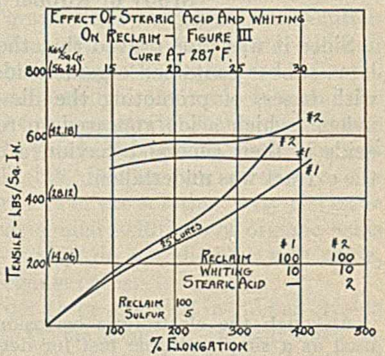


Table I—Effect of Softeners in Alkali Whole-Tire Reclaim—Digester Process

	No Oil (1)	No Oil (2)	4% Pine Tar (1)	4% Pine Tar (2)	4% Stearic Acid (1)	4% Stearic Acid (2)
	%	%	%	%	%	%
Acetone	8.25	8.38	8.63	9.64	7.23	7.41
Ash	18.14	18.26	17.76	17.90	16.83	16.80
Chloroform	25.40	24.90	29.82	28.07	25.98	25.15
Plasticity, *K*	5.73		4.68		6.01	

Reclaim 100, sulfur 5%

Cure at 141.6° C.	Tensile strength		Elong.	Set	Tensile strength		Elong.	Set	Tensile strength		Elong.	Set
Min.	*Kg./cm.*^{2}	*Lbs./in.*^{2}	%	%	*Kg./cm.*^{2}	*Lbs./in.*^{2}	%	%	*Kg./cm.*^{2}	*Lbs./in.*^{2}	%	%
15	50.1	713	420	23	59.4	844	435	22	44.5	634	387	15
20	43.8	623	390	15	55.0	780	410	16	39.6	564	325	11
25	37.7	536	367	12	43.8	623	340	13	37.8	538	350	12
30	37.1	528	360	12	46.0	654	340	12	35.4	503	317	11
35	40.5	576	370	10	48.2	685	370	15	36.8	524	320	10

STRESS-STRAIN

Elong. %	*Kg./cm.*^{2}	*Lbs./in.*^{2}	*Kg./cm.*^{2}	*Lbs./in.*^{2}	*Kg./cm.*^{2}	*Lbs./in.*^{2}
100	12.0	171	10.4	148	10.4	148
200	16.8	239	20.4	291	17.4	248
300	27.0	384	36.6	520	31.4	446

HEATER PROCESS—Table II shows physical test data on three reclaims prepared by the heater process. The fiber-free ground treads were heated for 16 hours at 130 pounds (9.1 kg. per sq. cm.) steam pressure without softener and with 5 per cent of pine tar and 5 per cent of stearic acid. The stock softened with pine tar approached proper consistency while the reclaim made without softener and the reclaim made with stearic acid were quite harsh. The reclaim using stearic acid was more plastic in its milling properties than the reclaim using no softener. It was smoother and more compact with less tack than the sample using pine tar although not so plastic.

Effect of Stearic Acid Added to Plasticized Rubber

The second use for stearic acid is for incorporation into the reclaimed rubber after devulcanization. After treatment in the digester, the plasticized rubber is washed, dried, and sent to the mill room for the refining, straining, and leaf sheeting operations. The softener may be added at any convenient

Table II—Effect of Softeners in a Heater Process Tire Reclaim

	No Softener				5% Pine Tar				5% Stearic Acid			
	Devulcanized 16 hours at 130 lbs. (9.1 kg. per sq. cm.)											
	%				%				%			
Acetone	12.20				12.86				12.76			
Ash	16.04				14.93				15.24			
Chloroform	18.39				22.07				24.60			
Specific gravity	1.132				1.125				1.127			
	Reclaim 100, sulfur, 5%											
Cure at 141.6° C.	Tensile strength		Elong.	Set	Tensile strength		Elong.	Set	Tensile strength		Elong.	Set
Min.	*Kg./cm.²*	*Lbs./in.²*	%	%	*Kg./cm.²*	*Lbs./in.²*	%	%	*Kg./cm.²*	*Lbs./in.²*	%	%
15	25.7	366	290	8	25.7	366	357	8	28.8	410	297	10
20	26.0	369	250	4	24.0	341	303	4	28.9	411	255	6
25	28.6	407	243	4	30.5	434	310	7	32.8	466	247	9
30	29.9	425	215	2	29.2	415	260	4	31.5	448	227	6
40	29.4	418	187	4	32.9	468	220	4	33.2	472	200	5
50	31.4	446	205	4	33.1	471	230	4	35.2	500	180	3
K			5.62				4.94				5.59	
Recovery, per cent			4.00				5.74				4.21	

time after washing. Prior to refining a softener may be added in an internal mixer to effect further plasticization or to facilitate dispersion of a pigment which is to be refined into the reclaim. The reclaim now has a low alkali content and the stearic acid in this case acts as such and imparts to the reclaim some very desirable properties. Approximately four volumes of various pigments were refined into a whole-tire reclaim with and without addition of stearic acid to determine the effect of stearic acid on physical properties, plasticity, etc.

Table III—Value of Stearic Acid in Reclaim for Activation Purposes in a Compound

	Stearic Acid Added to Compound	Stearic Acid Present in Reclaim
Smoked sheets	15	15
Reclaim, 2 per cent stearic acid	...	50
Reclaim, no stearic acid	49	...
Zinc oxide	5	5
Whiting	27.8	27.8
Sulfur	2	2
Captax	0.2	0.2
Stearic acid	1	...
	100.0	100.0

Cure at 141.6° C.	Tensile Strength		Elong.	Set	Tensile Strength		Elong.	Set
Min.	*Kg./cm.²*	*Lbs./in.²*	%	%	*Kg./cm.²*	*Lbs./in.²*	%	%
15	70.7	1007	480	33	75.5	1075	513	36
20	75.5	1074	480	35	77.6	1105	503	34
25	76.2	1085	460	33	79.4	1130	500	36
30	80.3	1142	480	36	82.4	1172	480	37
35	74.6	1062	440	33	76.9	1094	450	32
40	69.1	983	400	29	76.0	1082	437	33

Figure I illustrates the curing properties of two reclaims made from whole tires by the alkali process. In one case the reclaim was refined with no addition of pigment or softener on the warm-up mill and in the other case with 2 per cent of stearic acid added. The stearic acid improves the curing properties. The tensile strength is improved and the stress-strain curve indicates better reënforcing properties. The per cent alkalinity as NaOH after 48 hours' extraction was 0.30 per cent on the control and 0.24 per cent when stearic acid was added.

Figure II shows two reclaims containing 10 per cent of clay added prior to refining on the warm-up mill, with 2 per cent of stearic acid added in one case. The same improvement is noted as in Figure I. Figure III gives the same comparison as Figure II, except that whiting was added instead of clay. Figure IV shows the comparison with 7.5 per cent of carbon black added.

Figure V shows a comparison of plasticity coefficients of the eight reclaims, four with and four without stearic acid. Each stock containing stearic acid is more plastic than the one without stearic acid, the difference being less marked in the stocks containing carbon black. These plasticities were run on the day following the refining operation.

Table III shows a comparison of plasticity coefficients taken a week later as against plasticities taken the day after the refining operation. The recovery results were obtained by measurement of the increase in thickness of the plasticity disk during the 10 minutes following its removal from the Williams plastometer. It is expressed as percentage increase in thickness. This result is a measure of the nerve of the reclaim. The recovery or nerve is less in the stocks in which stearic acid was used. The reduction of nerve in reclaimed rubber improves the tubing and calendering properties of compounds in which it is used. Stearic acid is valuable for this purpose because it accomplishes this result without the production of further "tack."

Effect of Stearic Acid in Compounds Containing Reclaimed Rubber

Table IV gives a comparison of physical test data of two compounds containing stearic acid. In one case stearic acid was present in the reclaim and in the other case it was added in the compound. Physical tests indicate that stearic acid present in reclaimed rubber is valuable for activation of Captax.

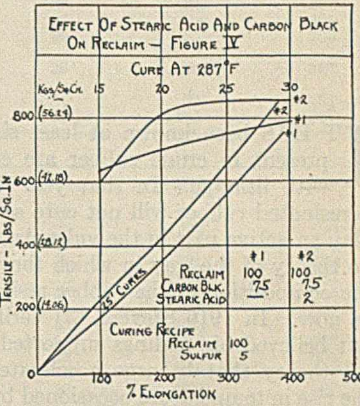
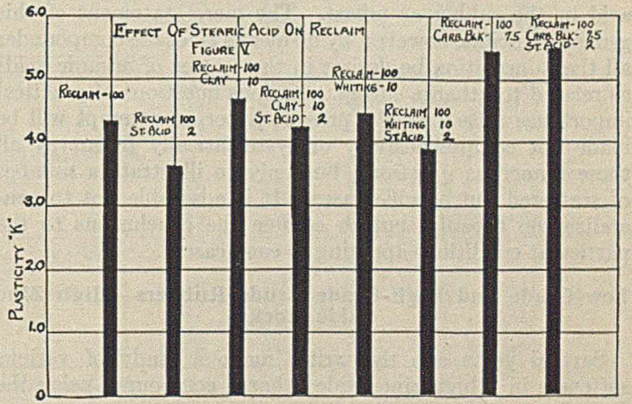


Table IV—Effect of Stearic Acid on Plasticity of Reclaimed Rubber

Stearic Acid and Pigment Added to Whole-Tire Reclaim 100	Plasticity *K*	Plasticity *K* after 1 Week	Recovery
None	4.32	4.86	4.17
Stearic acid 2	3.62	4.49	3.70
Clay 10	4.67	5.05	4.57
Clay 10, stearic acid 2	4.24	5.19	2.60
Whiting 10	4.45	4.57	3.85
Whiting 10, stearic acid 2	3.86	4.71	1.22
Carbon black 7.5	5.41	6.08	3.08
Carbon black 7.5, stearic acid 2	5.46	6.04	2.35

After plastizing, it is often desirable to add a softener on the mill to reduce excessive "tack" to metal rolls. Stearic acid reduces tack in plastic reclaims and gives stocks which have a minimum amount of nerve. They break down readily with little tendency to go to the back roll or become mushy and difficult to remove from the mill. The improvement in curing properties of reclaimed rubber produced by the addition of stearic acid indicates that the use of stearic acid in compounds containing reclaim would produce a similar im-



provement. This has been found to be true. In compounds containing substantial amounts of alkali process reclaim, a low sulfur and a high accelerator ratio, there is sometimes a rapid reversion causing blowing after the proper cure has been reached. Compounds containing stearic acid show less tendency to reversion under these conditions than compounds containing other softeners.

Conclusions

1—Stearic acid does not compare with other softeners in plasticizing efficiency when used in contact with vulcanized rubber scrap during devulcanization.

2—Stearic acid when added as a softener to devulcanized scrap on the mill prior to refining imparts properties which are very desirable. (*a*) Makes the reclaim batch more plastic, (*b*) improves tubing and calendering properties, (*c*) reduces nerve without production of excess tack, (*d*) improves curing properties (higher tensile strength, higher modulus, and improved molding properties) of reclaimed rubber, (*e*) when pigments are added it gives better dispersion with improved physical properties.

3—Stearic acid when used in compounds containing reclaimed rubber improves the curing properties of these compounds.

Stearic Acid in Litharge-Cured Rubber Compounds

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IT HAS been known at least since 1912 that the resins present in crude rubber are essential to vulcanization with litharge. In that year Weber (*4*) reported that deresinated rubber will not cure and concluded that "resins play an active part in the vulcanization;" but he formulated no theory of the way in which they function. At that time the composition of the rubber resins was not so well known as now. In 1916 Stevens (*3*) verified Weber's conclusions, but believed his findings supported the Esch and Auerbach (*2*) theory that litharge accelerated vulcanization through the rise in temperature occasioned by an exothermal reaction.

It is now well understood that resins promote vulcanization through their content of organic acid. It was proposed by Bedford and Winkelmann (*1*) in 1924 that litharge vulcanization proceeds by the following steps: (*a*) reaction of lead oxide with an organic acid (naturally present in the resin or added during the mixing) to form a rubber-soluble soap; (*b*) reaction of the lead soap with hydrogen sulfide to form a hydrosulfide salt or a hydrosulfide; (*c*) reaction of the latter with sulfur to form a disulfide and then a polysulfide; (*d*) decomposition of the (unstable) polysulfide to yield a very active form of sulfur—the ultimate vulcanizer. The polysulfide theory has been generally accepted as accounting adequately for the known facts.

It is clear, then, that the efficiency of litharge as an accelerator is absolutely dependent upon the existence of an organic acid in the rubber as mixed. The mere statement of this general principle, however, by no means gives the compounder all the information he desires in the matter of organic acids as related to litharge curing. Various questions of practical importance arise. In the present paper an attempt will be made not comprehensively or systematically to survey all these numerous questions, but only to illustrate a number of scattered but specific cases. It is advisable not to generalize too broadly, but to confine the conclusions to the particular conditions applying to each case.

Low-Grade and High-Grade Crude Rubbers—High Zinc Oxide Stock

Several years ago the writer made a study of various softeners in a high zinc oxide litharge compound, using the formula:

Rubber	100
Sulfur	8
Litharge	20
Zinc oxide	100
Softener	5

Two series of stocks were made up, one using a typical "high-grade" crude (smoked sheet) and the other a "low-grade" wild rubber (Lapori). Each series was master-batched up to the point of adding the various softeners, which were added to portions of the master batches on the laboratory mill. The stocks were vulcanized in the press at 141° C. (40 pounds steam) over a series of cures in order adequately to develop the optimum cure and to show the effect of the various softeners on the two grades of rubber. Stress-strains were determined on all the vulcanizates.

The results were entirely different for the two crudes, as will be seen from Tables I and II. In Table I the physical properties of the stocks of the Lapori series at their optimum cures (defined by maximum energy) are shown. While the control mix (without softener) came to an optimum in 150 minutes with a tensile of 2115 pounds per square inch, most of the softeners reduced the time to reach optimum and raised the properties at optimum. This table should not be used to draw fine distinctions between two given softeners, particularly where they are close together in the table. But the outstanding fact is that those softeners which are either acids or salts, or contain an acid, and which therefore can bring the lead into solution in the rubber as a salt, are the ones which significantly aided the cure.

On the other hand, in the corresponding data for the smoked sheet series we find no enhancement of cure by any of the softeners. As measured by time to reach optimum and (or) properties at optimum, most of the softeners inflicted some damage (slight or moderate). It should be noted, however, that this damage in the case of smoked sheet is distinctly less than the benefit conferred by the acid class of softeners on Lapori.

A further insight into the results themselves is furnished by Table II, giving the stress-strains for all the cures on both Lapori and smoked sheet compounded without and with 5 per cent stearic acid. The data for Lapori emphasize how far apart in their properties the control stock and the stearic acid stock are at a given cure. For example, on this basis stearic acid about doubled the modulus of Lapori. The presence of bloom up to 180 minutes without stearic and its disappearance between 60 and 90 minutes with stearic further confirm the accelerating effect of this acid.

In sharp contrast to these are the results on smoked sheet. Here there is, if anything, a retardation of cure by stearic and at a given cure the modulus is greatly lowered, although the tensile is not much affected. This serves to emphasize that the observed stiffening of the Lapori vulcanizate is the net result of two opposing tendencies: (*a*) a stiffening due to the enhancement of the cure, consequent in turn upon the acid bringing more lead into the available, soluble form;

Table I—Physical Data for Cures of Maximum Resilient Energy of Litharge-Rubber Stocks Activated with Various Softeners. Cured in Press at 141° C. (40 Pounds Steam)

SOFTENER	CURE OF MAX. ENERGY	TENSILE AT ELONGATION OF:		TENSILE	ELONG.	SUBPERMANENT SET	T. P.	ENERGY
		300%	600%					
	Min.	*Lbs./sq. in.*		*Lbs./sq. in.*	%	%		*Ft-lbs./cu. in.*
LITHARGE–LAPORI STOCK								
Rubberite	30	455	2327	3200	685	51	219	546
Benzoic acid	30	445	2270	2660	640	36	170	433
Rosin	60	395	2090	3252	705	54	229	542
Zinc stearate	60	475	2310	3000	670	53	200	510
Pine tar	60	477	2585	3067	645	48	198	499
Rosin oil	60	495	2625	2875	630	46	181	464
Zinc benzoate	60	585	2790	2817	605	46	170	457
Oleic acid	60.	480	2542	2850	630	52	180	446
Stearic acid	60	450	2312	2622	635	44	166	419
Phenol	90	642	2267	2535	650	38	164	493
Hardwood pitch	90	537	2030	2232	630	32	141	405
Lead phenolate	90	417	1545	2142	675	42	144	382
Cumar, grade 310	90	305	1157	1760	705	35	124	323
n-Butyl salicylate	90	347	1365	1837	670	32	123	320
Glycerol	120	195	730	1150	705	38	81	208
Nil (control)	150	487	1695	2115	655	29	138	387
Cumar, grade 315	150	397	1367	1540	640	31	95	291
Cumar, varnish grade	> 150	482	1640	1890	640	33	121	357
LITHARGE–SMOKED SHEET STOCK								
Nil (control)	15	562	2970	3567	665	36	237	635
Hardwood pitch	15	627	2977	3355	655	31	220	620
Cumar, grade 310	15	530	2850	3427	660	37	226	590
Cumar, varnish grade	15	517	2782	3347	660	37	221	574
Zinc stearate	20	420	2242	3762	730	54	275	660
n-Butyl salicylate	20	577	2795	3385	670	35	226	622
Lead phenolate	30	1085		3542	590	45	209	645
Cumar, grade 315	30	675	3062	3670	650	49	239	634
Oleic acid	30	753	3565	3665	610	52	223	610
Phenol	30	902	3527	3527	600	43	212	608
Rubberite	30	740	3280	3510	620	42	218	601
Zinc benzoate	30	655	3102	3462	630	42	218	579
Rosin oil	30	730	3192	3360	615	42	206	567
Stearic acid	30	580	3067	3430	635	52	217	564
Benzoic acid	30	620	3240	3540	620	42	219	562
Glycerol	30	560	2480	3015	650	49	198	510
Pine tar	45	718	3075	3725	650	46	242	654
Rosin	45	715	3220	3485	625	44	217	597

Conversion factor for tensiles: 1 lb. per sq. in. = 0.0703 kg. per sq. cm.
Conversion factor for energies: 1 ft-lb. per cu. in. = 0.84 kg-cm. per cc.

Table II—Effect of 5 Per Cent Stearic Acid in Litharge Stock Loaded with Zinc Oxide

CURE AT 141° C.	TENSILE AT ELONGATION OF:								TENSILE	ELONG.	SUBPERMANENT SET	T. P.	ENERGY	BLOOM[a]
	100%	200%	300%	400%	500%	600%	700%	800%						
Min.	*Lbs./sq. in.*								*Lbs./sq. in.*	%	%	*Ft-lbs./cu. in.*		
LAPORI WITH NO STEARIC ACID														
60	85	150	235	350	595	1000	1520		1595	715	32	114	284	+
90	94	165	282	420	700	1062			1625	690	24	112	283	+
120	107	222	372	555	920	1402			1872	670	25	125	335	+
150	137	300	487	740	1090	1695			2115	655	29	138	387	+
180	145	280	465	692	1062	1652			2000	650	27	130	365	+
LAPORI WITH 5 PER CENT STEARIC ACID														
30	137	212	320	520	1022	1935			2702	675	45	182	410	+
60	192	300	450	717	1347	2312			2622	635	44	166	419	+
90	232	367	520	837	1477				2050	565	40	116	320	−
SMOKED SHEET WITH NO STEARIC ACID														
10	105	257	425	767	1407	2395			3180	675	36	214	521	
15	167	332	562	1065	1880	2970			3567	665	36	237	635	
20	197	400	652	1107	1940	2992			3572	655	39	234	633	
SMOKED SHEET WITH 5 PER CENT STEARIC ACID														
10	85	130	202	320	575	1110	1922	2922	3140	825	51	259	547	
15	157	210	335	570	1117	1982	3055		3135	710	45	222	517	
20	165	270	397	645	1272	2222	3365		3365	700	48	235	554	
30	238	385	580	1025	1868	3067			3430	635	52	217	564	
45	277	430	665	1113	1970	3040			3040	600	53	182	498	

[a] A plus sign (+) means sulfur bloom present, a minus sign (−) means bloom absent.

(*b*) a softening quite analogous to that of any non-acidic softener such as mineral oil or mineral rubber. What the net result will be in a given case depends upon the magnitude of the two component effects. Where, as in many low-grade crudes, the natural resin content is low or deficient in acid, an addition of stearic acid, oleic acid, pine tar, or similar material greatly accelerates otherwise slow curing and enhances otherwise low properties; on the other hand, where the natural acid content is relatively high, a further addition shortens the time of cure little or none (it may retard) and the resulting observed effect is likely to be a distinct softening at a given cure.

The effect of the softeners on set should be noted. This was measured on specimens broken in the course of determining stress-strains and was taken from 5 to 10 seconds after the break. With few exceptions set was increased by the softeners, this being true for both grades of rubber but more marked with smoked sheet. This phenomenon is doubtless closely allied to softening action, both being expressions of the reduction of elastic properties. Hardwood pitch—which however only moderately enhanced the curing of Lapori—in the case of both grades of crude had about the least effect on set.

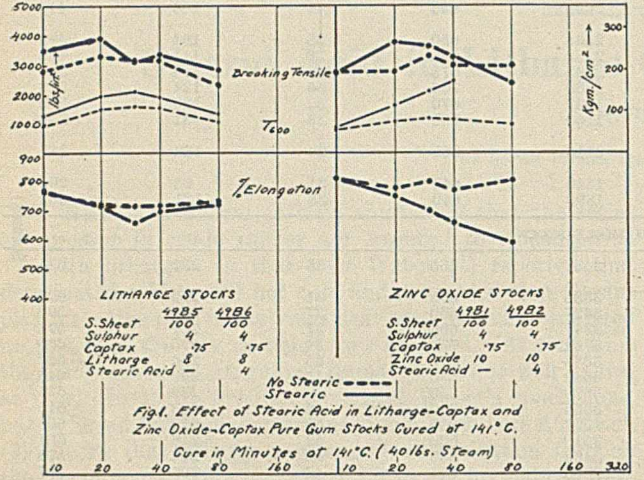

Fig. 1. Effect of Stearic Acid in Litharge-Captax and Zinc Oxide-Captax Pure Gum Stocks Cured at 141° C.

There is little doubt in the writer's mind that a smaller quantity of softener than used throughout the present series would, in the case of the more active ones at least, have furnished maximum activation. It is clear that it is useless to go beyond a certain limit which, in so far as curing considerations are concerned, is perhaps nil for standard smoked sheet and for the present type of formula. In the case of Lapori, perhaps from 2 to 3 per cent of stearic acid would have yielded maximum activation. To exceed the limit for full activation means to increase the softening action on the vulcanizate.

Stearic Acid in a Pure Gum and a Gas Black Stock

In the remaining cases we are dealing with smoked sheet, which normally does not require an addition of acid in so far as enhancement of cure with litharge is concerned. Tables III and IV illustrate this, Table III showing results for a pure gum mix and Table IV for a gas black stock. The pure gum stock (49A2) with 1 per cent of stearic acid follows closely in its properties that with no added acid (49A1), and has an identical rate of cure. There is a very slight softening effect on the part of the stearic.

With gas black stearic improved the tensile significantly. As the object was to determine not the dispersing action of the stearic on the black, but rather the effect on curing, the softener was so added as to minimize any benefit it might confer on dispersion; i. e., the rubber, sulfur, black, and litharge were master-batched and 4 per cent stearic was subsequently milled into half of this batch to yield 49A5. There is meager, and only meager, evidence of enhancement of cure by the stearic. The increase in tensile at all cures, on the other hand, is distinct; it is due to increased elongation (not stiffness), and probably represents improved dispersion, notwithstanding the precaution to the contrary.

Why have we only a slight softening of the gas black stock by 4 per cent stearic (assuming that the softening exhibited by Table IV is significant at all), while in Table II for smoked sheet 5 per cent stearic cut the modulus in half; and why with the black have we evidence of (slight) activation of cure but with zinc oxide appreciable retardation by the stearic added? Two possible explanations suggest themselves: (1) With gas black an appreciable part of the stearic may be adsorbed, leaving only the free part to soften the rubber phase. If this is the case, then conceivably there was a moderate deficiency of free organic acid in 49A4 which was made up in 49A5 by the added acid. A much smaller adsorptive effect is to be expected from the zinc oxide. (2) Probably the dispersion of the black was improved by the stearic, introducing thus a stiffening factor which would operate against the softening action of the stearic on the rubber phase. If so, with zinc oxide there would be no corresponding stiffening factor consequent upon improved dispersion and higher reënforcement, since zinc oxide disperses readily without added stearic.

Stearic Acid and Litharge in Conjunction with Mercaptobenzothiazole

The observations made above are on stearic acid in stocks accelerated by litharge. It is of interest to note what obtains when litharge is used in conjunction with an organic accelerator as an "activator," analogously to zinc oxide. For this purpose mercaptobenzothiazole (Captax) was employed, since (*a*) litharge strongly activates this accelerator and (*b*) it is well known that when zinc oxide is used as the activator a full curing propensity is highly dependent on stearic acid, especially in the presence of gas black.

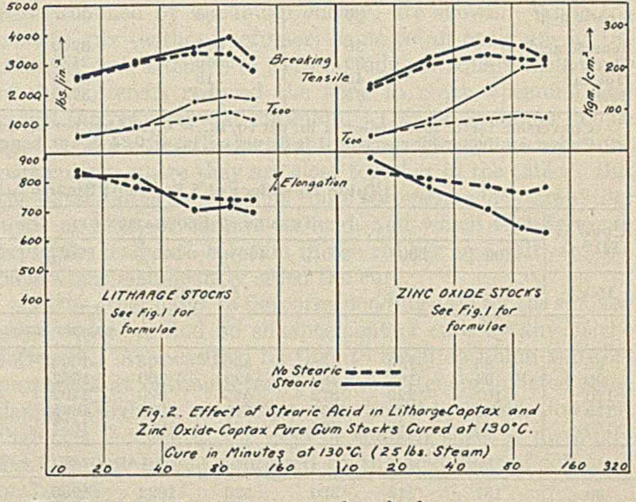

Fig. 2. Effect of Stearic Acid in Litharge-Captax and Zinc Oxide-Captax Pure Gum Stocks Cured at 130° C.

Two base stocks were master-batched:

Pure Gum Base		Gas Black Base	
Smoked sheet	100	Smoked sheet	100
Sulfur	4	Sulfur	4
Captax	0.75	Captax	0.75
		Gas black	45

Each stock was then subdivided into four parts each and to these portions the following additions were made:

Litharge	8
Litharge Stearic acid	8 4
Zinc oxide	10
Zinc oxide Stearic acid	10 4

Thus there were studied all the combinations which arise from varying the following items:

Reënforcement (and concomitant adsorptive effects)	Pure gum *vs.* high gas black
Activation	Litharge *vs.* zinc oxide
Acidic softener (added)	Stearic absent *vs.* stearic present

Table III—Effect of 1 Per Cent Stearic Acid in a Pure Gum Litharge Stock

FORMULAS	49A1	49A2
Smoked sheet	100	100
Sulfur	5	5
Litharge	15	15
Stearic acid	...	1

CURE AT 141° C.	TENSILE AT ELONGATION OF:								TENSILE	ELONG.	T. P.	ENERGY
	100%	200%	300%	400%	500%	600%	700%	800%				
Min.	Lbs./sq. in.								Lbs./sq. in.	%		Ft-lbs./cu. in.
49A1—NO STEARIC ACID												
10	64	86	128	214	343	621	1220	2135	2135	800	171	312
20	65	119	195	303	541	1090	2110		2895	765	222	416
30	86	150	237	387	667	1290	2580		3120	755	236	473
40	90	157	290	470	883	1690			2840	695	197	407
80	90	156	279	458	727	1340	2390		2435	705	172	364
49A2—1 PER CENT STEARIC ACID												
10	66	88	154	220	341	637	1230	2175	2195	805	177	326
20	66	109	174	304	511	1045	2055		2830	760	215	375
30	87	152	238	335	606	1230	2490		3075	740	228	417
40	85	171	299	499	792	1645	2890		2890	700	202	411
80	65	139	286	408	667	1265	2365		2450	720	176	374

Table IV—Effect of 4 Per Cent Stearic Acid in a Gas Black Litharge Stock

FORMULAS	49A4	49A5
Smoked sheet	100	100
Sulfur	5	5
Litharge	15	15
Gas black	45	45
Stearic acid	...	4

CURE AT 141° C.	TENSILE AT ELONGATION OF:							TENSILE	ELONG.	T. P.	ENERGY
	100%	200%	300%	400%	500%	600%	700%				
Min.	Lbs./sq. in.							Lbs./sq. in.	%		Ft-lbs./cu. in.
49A4—NO STEARIC ACID											
10	128	330	771	1430	2240	3140		3450	645	223	663
15	183	438	1035	1790	2755	3725		3890	610	237	704
20	264	622	1360	2260	3385	4285		4360	610	265	872
30	336	822	1610	2485	3625			4225	560	237	785
40	444	981	1850	2780	3835			4350	550	239	835
60	430	1050	1970	3040	4035			4035	500	202	709
80	490	1155	2080	3195				3980	475	189	668
49A5—4 PER CENT STEARIC ACID											
10	121	282	684	1295	2110	2975	3900	4060	715	291	834
15	157	395	880	1585	2540	3480	4485	4485	700	314	940
20	233	602	1240	2060	3070	4100		4520	640	290	915
30	322	798	1640	2610	3745			4460	570	254	843
40	414	1005	2030	3035	4140			4550	545	248	877
60	505	1315	2160	3320				4265	485	207	739
80	424	1110	1930	3030	4145			4145	500	207	718

Table V—Effect of Stearic Acid on Litharge-Captax and Zinc Oxide-Captax Pure Gum Stocks, Cured at 141° C. (40 Pounds Steam)

CURE	TENSILE AT ELONGATION OF:								TENSILE	ELONG.	T. P.	ENERGY
	100%	200%	300%	400%	500%	600%	700%	800%				
Min.	Lbs./sq. in.								Lbs./sq. in.	%		Ft-lbs./cu. in.
49B5—8 PER CENT LITHARGE, NO SETARIC ACID												
10	64	115	158	285	495	947	1960		2800	765	214	381
20	82	142	244	406	670	1500	2800		3300	725	239	435
30	83	144	248	433	742	1600	2900		3150	715	225	427
40	96	135	250	425	750	1540	2850		3150	720	227	435
80	79	128	227	345	582	1045	1960		2320	735	171	344
49B6—8 PER CENT LITHARGE, 4 PER CENT STEARIC ACID												
10	85	128	223	330	617	1275	2390		3490	770	269	493
20	85	180	298	489	900	1950	3600		3900	715	279	522
30	123	204	337	531	1000	2100			3100	660	205	400
40	89	203	334	527	925	1900	3350		3350	700	235	471
80	79	158	276	423	710	1340	2480		2835	725	206	407
49B1—10 PER CENT ZINC OXIDE, NO STEARIC ACID												
10	66	99	154	253	450	792	1515	2705	2745	810	222	413
20	89	125	206	331	572	1050	1950		2800	780	218	437
30	68	135	225	360	600	1140	2100	3300	3300	800	264	523
40	63	157	241	380	600	1120	2050		2995	770	231	446
80	64	127	212	339	581	953	1715	2920	2965	805	239	466
49B2—10 PER CENT ZINC OXIDE, 4 PER CENT STEARIC ACID												
10	70	93	163	279	465	860	1615	2600	2720	810	220	426
20	92	161	253	402	758	1605	2870		3750	750	281	531
30	93	185	324	566	1040	2080	3610		3610	700	253	508
40	114	239	432	682	1270	2450			3250	660	215	473
80	106	212	405	681	1300				2380	590	140	309

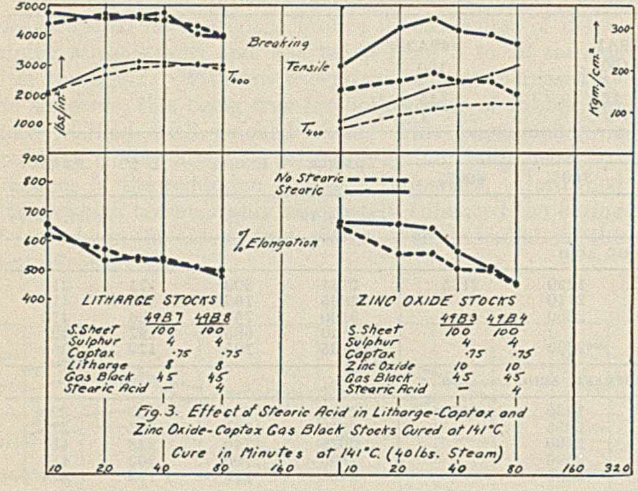

Fig. 3. Effect of Stearic Acid in Litharge-Captax and Zinc Oxide-Captax Gas Black Stocks Cured at 141°C

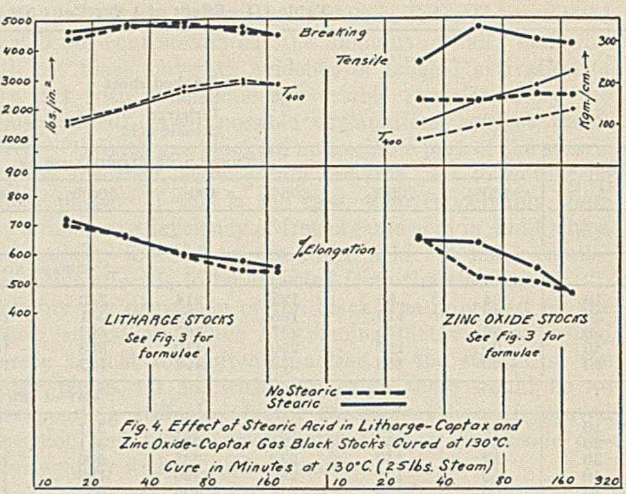

Fig. 4. Effect of Stearic Acid in Litharge-Captax and Zinc Oxide-Captax Gas Black Stocks Cured at 130°C.

It will be noted that here, as in an earlier experiment, the stearic was added after the milling of the gas black into the gum, in order to influence dispersion in a minimal way. These eight stocks were then press-cured over a range at 141° C. (40 pounds steam) and at 130° C. (25 pounds steam) and stress-strains were determined on all vulcanizates.

The complete physical data including tensile product (T. P.) and energy are displayed in Tables V to VIII, and certain of these data are, for readier assimilation, graphed in Figures 1 to 4. In the graphs will be found breaking tensiles, elongations, and moduli, the latter being represented by tensiles at 600 per cent elongation (T_{600}) for pure gum stocks and at 400 per cent elongation (T_{400}) for gas black stocks. Each graph is based directly on one of the tables—for example, Figure 1 on Table V, 2 on VI, etc. The curves obtained with and without stearic acid (other conditions being constant) are superimposed in the same space (stearic present represented by solid lines, stearic absent by broken lines). In this way the effect of stearic acid in a given set of conditions is observable at a glance. In reading the graphs due account of the logarithmic time scale should be taken.

The outstanding result is that the behavior of the litharge-Captax combination toward stearic acid is in sharp contrast to that of the zinc oxide–Captax combination. The former is seen to be relatively independent of added stearic for its activity, coming to approximately full properties without the acid; the latter is highly dependent on, and produces its maximum results only with, added acid. These general conclusions hold for both the pure gum and the gas black stocks, though more pronounced for the black.

Examining the graphs in detail we find as follows: In Figure 1 (pure gum mixes cured at 141° C.), in the case of litharge the tensile and modulus are appreciably raised by stearic acid but the properties as a whole are not changed so radically as in the case of zinc oxide. With the latter we have an otherwise low modulus greatly raised and an otherwise high elongation considerably lessened, especially in the longer cures. These two effects on modulus and stretch influence the tensile oppositely so that it has not undergone any more change than it did with litharge. Notwithstanding the near-identity in the influence of stearic acid on breaking tensile in the case of the pure gum litharge and pure gum zinc oxide stocks, the dependence of modulus and elongation in the case of zinc oxide constitutes a difference in vulcanizing behavior which is significant from the practical standpoint certainly, and from the theoretical perhaps. Figure 2, displaying proper-

Table VI—Effect of Stearic Acid on Litharge-Captax and Zinc Oxide–Captax Pure Gum Stocks, Cured at 130° C. (25 Pounds Steam)

Cure	Tensile at Elongation of:								Tensile	Elong.	T. P.	Energy
	100%	200%	300%	400%	500%	600%	700%	800%				
Min.	*Lbs./sq. in.*								*Lbs./sq. in.*	*%*		*Ft-lbs./cu. in.*
49B5—8 PER CENT LITHARGE, NO STEARIC ACID												
15	48	72	120	169	313	566	1095	2075	2555	840	215	362
30	72	119	167	286	452	906	1980		3050	785	240	427
60	68	137	205	319	557	1145	2265		3390	750	254	415
90	88	142	230	394	689	1380	2690		3370	740	249	457
120	74	128	214	363	599	1095	2375		2780	735	204	380
49B6—8 PER CENT LITHARGE, 4 PER CENT STEARIC ACID												
15	66	88	131	219	339	612	1245	2175	2600	825	214	365
30	83	124	187	280	457	861	1765	2700	3110	820	255	474
60	95	167	286	443	822	1735	3515		3570	705	247	457
90	82	174	298	432	893	1905	3610		3900	715	279	513
120	97	146	267	473	837	1805			3200	695	222	425
49B1—10 PER CENT ZINC OXIDE, NO STEARIC ACID												
15	51	76	101	164	304	557	1035	1845	2155	830	179	317
30	73	97	170	291	485	896	1780	2905	2930	805	236	449
60	66	131	219	339	558	1085	2100		3260	780	254	466
90	89	134	223	400	656	1220	2355		3110	755	235	450
120	74	148	245	393	664	1140	2260		3075	775	238	483
49B2—10 PER CENT ZINC OXIDE, 4 PER CENT STEARIC ACID												
15	48	72	96	169	277	506	933	1555	2290	880	202	368
30	67	123	202	290	548	1085	2010		3175	775	246	439
60	97	193	338	554	1020	2170	3740		3740	700	262	520
90	116	232	419	709	1425	2840			3535	635	225	453
120	129	269	456	773	1590	2900			3155	620	196	439

Table VII—Effect of Stearic Acid on Litharge-Captax and Zinc Oxide-Captax Gas Black Stocks, Cured at 141° C. (40 Pounds Steam)

CURE	TENSILE AT ELONGATION OF:						TENSILE	ELONG.	T. P.	ENERGY
	100%	200%	300%	400%	500%	600%				
Min.	*Lbs./sq. in.*						*Lbs./sq. in.*	%		*Ft-lbs./cu. in.*
49B7—8 PER CENT LITHARGE, NO STEARIC ACID										
10	215	503	1077	2095	3085	4100	4395	620	273	823
20	297	737	1585	2660	3800		4710	570	269	843
30	345	864	1780	2910	4040		4565	535	245	785
40	364	892	1830	2980	4100		4500	540	243	820
60	349	923	1860	3010	4170		4290	510	219	721
80	324	838	1740	2865	3930		3930	500	197	645
49B8—8 PER CENT LITHARGE, 4 PER CENT STEARIC ACID										
10	236	549	1175	2060	3100	4160	4750	655	311	971
20	305	876	1790	2970	4150		4530	530	240	777
30	345	934	1970	3120	4305		4670	545	255	878
40	352	957	1900	3075	4200		4755	530	252	811
60	350	941	1850	3025	3980		4020	510	205	713
80	350	914	1850	2995			3900	480	187	614
49B3—10 PER CENT ZINC OXIDE, NO STEARIC ACID										
10	90	233	466	834	1345	1880	2135	650	139	409
20	156	390	750	1300	2000		2475	555	137	402
30	191	450	850	1500	2250		2750	560	154	468
40	209	490	969	1645	2440		2480	505	125	388
60	267	554	985	1720	2465		2465	500	123	397
80	280	561	1040	1700			2035	455	93	313
49B4—10 PER CENT ZINC OXIDE, 4 PER CENT STEARIC ACID										
10	123	288	586	1095	1740	2460	2975	665	198	569
20	234	566	1085	1840	2800	3765	4270	655	280	885
30	318	723	1355	2260	3310	4385	4540	625	284	939
40	400	830	1505	2405	3505		4150	565	234	765
60	408	929	1735	2695	3775		4020	510	205	670
80	457	1105	1980	2980			3700	450	167	558

Table VIII—Effect of Stearic Acid on Litharge-Captax and Zinc Oxide-Captax Gas Black Stocks, Cured at 130° C. (25 Pounds Steam)

CURE	TENSILE AT ELONGATION OF:							TENSILE	ELONG.	T. P.	ENERGY
	100%	200%	300%	400%	500%	600%	700%				
Min.	*Lbs./sq. in.*							*Lbs./sq. in.*	%		*Ft-lbs./cu. in.*
49B7—8 PER CENT LITHARGE, NO STEARIC ACID											
15	159	375	827	1590	2460	3380	4370	4370	700	306	915
30	224	576	1200	2120	3105	4200		4815	665	320	1021
60	290	791	1670	2720	3905			4885	595	291	967
120	376	959	1875	2935	4070			4520	545	246	843
180	352	868	1745	2825	4000			4450	540	240	790
49B8—8 PER CENT LITHARGE, 4 PER CENT STEARIC ACID											
15	146	376	794	1445	2380	3310	4385	4640	720	334	962
30	217	578	1125	1995	2980	4120		4870	660	321	971
60	287	772	1542	2560	3700	4740		4740	600	285	936
120	370	970	1845	2840	3970			4725	575	272	939
180	365	942	1805	2810	3900			4445	555	247	847
49B3—10 PER CENT ZINC OXIDE, NO STEARIC ACID											
15	Very porous										
30	115	253	518	892	1480	1985		2265	655	148	452
60	187	453	825	1370	2000			2215	520	116	355
120	230	570	1020	1650	2400			2440	505	123	399
180	330	725	1210	1910				2425	465	113	386
49B4—10 PER CENT ZINC OXIDE, 4 PER CENT STEARIC ACID											
15	Porous										
30	159	398	829	1455	2170	2995		3525	650	229	678
60	279	690	1320	2180	3180	4310		4710	635	299	948
120	415	979	1765	2755	3905			4280	550	235	826
180	515	1130	2085	3215				4140	465	193	644

ties on the same four stocks as Figure 1, but cured at 131° C., leads to the same conclusions.

The conclusion, discernible on analysis of the pure gum results, that there is a significant difference in the behavior toward stearic acid of litharge-Captax and of zinc oxide-Captax stocks, is confirmed by the data for the gas black mixes. Both Figure 3 (141° C. cures on gas black stocks) and Figure 4 (130° C. cures) show an almost complete lack of influence by added stearic when litharge is used for activation but a marked dependence on the acid when zinc oxide is used. For example, at 141° C. either with or without stearic, the litharge-activated stocks reached a tensile of 4400 to 4700 early in the cure and maintained this value approximately unchanged to the 40-minute cure. On the other hand, while the zinc oxide stock with stearic showed a maximum tensile of 4540 reached in the 30-minute cure, without stearic only 2750 was reached (also in 30 minutes). Similarly, at 130° C. the litharge stocks, with or without stearic, maintained a tensile of approximately 4400 to 4900 over the curing range of 15 to 180 minutes. With zinc oxide and stearic a maximum of 4710 was reached in 60 minutes, but without stearic a maximum of only 2440 was reached (in 120 minutes).

There is obviously some, at least quantitative, difference in the mechanism of mercaptobenzothiazole acceleration in conjunction with the two oxide activators, a difference which is accentuated when to the gum there is added an agent which powerfully adsorbs the organic acid and (or) the accelerator. Of what this difference in mechanism consists we shall not attempt to say. Possibly it has to do with the extent to which lead and zinc, respectively, are made available to the mercaptan so as to permit of mercaptide formation, this in turn being influenced by the solubilities or mobilities of lead stearate and of zinc stearate; or, on the other hand, it might have to do with a difference in the chemistry of the lead and of the zinc mercaptides after their formation.

From the practical standpoint, a compound formulated along the line of 49B7 offers desirable qualities as a tread stock including high physical properties maintained over a wide range of cures. This sort of compound would appear also to be adapted to the present-day tendency toward low-temperature cures, with the advantage which that practice has of minimizing the damage to the rubber by heat. Because the litharge-Captax tread stock cures fully without the addition of stearic acid, it is not to be inferred that none should be added. That depends on requirements other than curing which may demand this ingredient, including obtaining a proper dispersion of the black and a desirable plasticity for tubing or calendering. But the point is that the stearic can be regulated in whatever way satisfies these other considerations with the assurance that curing requirements will have been met incidentally. Possibly in this way the amount of stearic used in general practice in a tread could be reduced, resulting in a lessened tendency toward stearic acid blooming.

Summary

Although an organic acid is essential to vulcanization with litharge, smoked sheet usually has enough natural acid for full activation. For example, when 5 per cent stearic acid (or similar softeners) was added to a standard smoked sheet in a high zinc oxide stock the properties were lowered. On the other hand, a "low-grade" rubber, Lapori, was greatly improved in a high zinc oxide formula by stearic and by other acids.

Acidic softeners in a high zinc oxide stock increased set, even when they promoted vulcanization.

In a pure gum litharge formula with smoked sheet, 1 per cent stearic had but little effect, while in a high gas black formula, 4 per cent stearic raised the tensile (probably due to improved dispersion) but had no marked effect on rate of cure.

When litharge was used as the activator for mercaptobenzothiazole, stearic acid had but little effect either in pure gum or high gas black stocks. On the contrary, when zinc oxide was used proper curing was highly dependent on stearic, especially with gas black. The litharge-mercaptobenzothiazole compounds with gas black in tread stock proportions, either with or without stearic, yielded a high tensile over a wide range of cures.

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[End of Symposium]

Economic Factors in Chemical Plant Location[1]

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IN A STUDY of the development of chemical and metallurgical industry in the United States, the first generalization is not so much the tendency for the centralization of industry, although that is the most obvious, but the fact that industry is continually migrating and that this migration is due to the influence of certain definite factors of plant location. The remarkable growth of American industries in a period of scarcely more than one hundred years is marked by the constant migration of industry from points of centralization to other favorable points. Profound changes are especially notable in the essentially technical industries, such as iron and steel, fertilizer, glass, coke, alkali, paper and wood pulp, coal-tar products, paint and varnish, sulfuric acid, and soap. These are usually classed as basic industries in that they demand sources of especially cheap power, proximity to raw materials, or an advantageous distribution, because the products are to be sold on a highly competitive market.

Migration of Different Classes of Industries

Before discussing the factors of plant location, I wish to correct some commonly accepted ideas which are prevalent in this connection. There are, for instance, arbitrary statements made which seem to apply to certain industries. It has been said that in the iron industry the ore goes to the fuel; that in carbide, abrasive, and aluminum manufacture the industry goes to cheap hydroelectric power; that the measure of sulfuric acid manufacture is local consumption; and that soda ash and caustic industry must sit on top of a salt mine. But these views are often superficial. The editor of the *Executives Magazine* (Vol. 12, No. 5, 1928) divides industries into three classes—the raw material industries, the competitive industries, and the population industries. Of the raw material industries he remarks, "industries which come to a region because the existence of heavy raw materials there makes it necessary to build plants on the ground." It is hardly ever true that industries come to a region because of the existence of raw materials. An examination of industrial location will show other factors are usually more important.

Basic Industries—Basic industries whose raw material is, for the most part, not processed and whose products in the main are the raw materials for other industries must, to succeed, locate near cheap fuel or cheap power. It is true that major raw materials must be obtainable (1) advantageously as to quality and price, or at least (2) on a competitive basis with the same industries in other localities; but these two factors alone will not serve to establish a basic industry, for basic industries demand cheap fuel and advantageous raw materials in order to compete in the national market. It is

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necessary, therefore, that the plant be located satisfactorily in reference to those industries manufacturing the same product and which are in direct competition with this industry, and also in reference to the consumer industries which are regular purchasers of its product. Again this editor says of the competitive industries: "The competitive industries, which employ 60 per cent of the workers of the United States and which, so far as price and raw materials are concerned, can go anywhere." To such a statement I cannot agree. No industry, much less a competitive one, "can go anywhere."

INTERMEDIATE INDUSTRIES—Intermediate industries, which probably include this author's "competitive industries," are those industries whose major raw materials have already been processed and which are dependent, to a degree, upon procuring these processed materials from the local producers or at least in a competitive market from outside sources. An intermediate industry, to succeed, must have favorable connections with local producers or purchase in a highly competitive market, and it must be able to sell to advantage in at least a portion of the national market.

TRIBUTARY INDUSTRIES—Those industries are tributary whose raw materials may be either primary or secondary, but whose sources of fuel and materials are not advantageous as compared with outside competition. A tributary industry, to succeed, should have an advantageous market locally, due to freight rates, and a limited favorable area due to freight differentials.

Position of Chemical Industry

In commenting on the position of chemical industry in the industrial structure of the United States, *Chemical and Metallurgical Engineering* (Vol. 34, No. 1, 1927) says editorially:

> A decentralizing influence has been at work, particularly since the war, and many established centers of certain industries have felt the effect of an industrial migration brought on by excessive costs of transporting raw materials and manufactured products, competitive bidding for labor and other of the disadvantages of a congested industrial district. Manufacturing is taking on a national character and consequently the market for chemicals is broadening to cover practically the whole of the United States.

Factors Influencing Plant Location

From a study of the migration of a number of industries, a second generalization might also be made, and one which executives of big business are just beginning to realize. That is, that increasing the capacity of a plant, ruthless competitive methods, and well-organized sales forces are helpless in preventing the migration of industry. To meet this migration it becomes necessary to establish branch plants in these migration centers or, what is better, to determine the logical migration points by industrial engineering research, and to forestall such competition by entering the field before independent competition has already preëmpted it. Such being the present trend, it is often the duty of a plant engineer to study the economics of his special branch of industry in order to determine the proper location for one or more branch plants. Briefly, there are twelve factors involved in plant location. The first five factors concern themselves chiefly with production; the others affect either distribution or overhead.

(1) RAW MATERIALS—Raw material sources may be local, favorable, or competitive, and are valuable to a community because of quality, reserve, proximity, and source of competitive material. Raw materials have really no geographical limitation, but are tributary to a certain district, where economic conditions, such as initial cost and freight rates, are more favorable than in other points of similar manufacture.

(2) LABOR—The supply and cost of labor involves such items as kind, nationality, quantity, diversity, intelligence, existing wage scales, and efficiency. In general, wages are lower in the country than in large cities. At present wages are lower in the Southern states than in the North Atlantic and the Mississippi Valley states. On the other hand, in quantity, diversity, intelligence, and efficiency, the labor in the cities will be found better than in the country. Labor of certain nationalities is more dependable, intelligent, and efficient than that of others.

(3) FUEL—The third factor in plant location is fuel, its kind, thermal efficiency, reserve, etc. The kinds of fuel are coal, coke, oil, and gas. Certain of these are more flexible than others. When they are in competition with each other, lower prices with higher thermal efficiency is the usual result.

(4) POWER—Power may usually be classed as hydroelectric or steam-generated power. The city with cheap hydroelectric power has a wonderful talking point for industrial development, but steam power plants are fast equaling hydroelectric performance, and Diesel engine installations, where fuel oil sells at less than 3.5 cents per gallon, are furnishing power at less than 6 mills per kilowatt-hour.

(5) WATER—To more than 75 per cent of the basic industries water is one of the governing factors in plant location; and quantity, analysis, and costs are the chief points considered.

(6) TRANSPORTATION FACILITIES—Where a city has more than one railroad, or, better still, railroads and barge or steamship lines, the freight competition occasioned by these several transportation facilities makes for lower freight rates, efficiency, and service.

(7) FREIGHT RATES—The larger the territory favorable to certain districts due to favorable freight rates, and the larger the population reached in this territory, the more important that district becomes as a potential industrial center.

(8) MARKETS—Markets are defined as local, favorable, competitive, and national. The local area is the population served by reason of plant location. The favorable area is that which an industry can serve by reason of low-cost production and freight rates. The competitive area is the area in which the industry must compete on equal, or nearly equal, terms with like industries in other localities. The national area is that in which, by reason of certain advantages in fuel, power, or raw materials, an industry expects to compete in spite of adverse freight rates.

(9) CLIMATE—The seasonal range, precipitation, humidity, wind, etc., which go to make the climate of a certain district are factors that often enter directly into manufacture. If not, they often affect plant location for purely personal and psychological reasons.

(10) TAXES AND CORPORATION FEES—Many cities handicap themselves by high tax rates. High corporation fees have often kept industries out of certain states. Chambers of commerce may well examine tax rates and corporation fees in their localities with a view to making them at least as reasonable as are found in the more developed industrial regions.

(11) MUNICIPAL RESTRICTIONS—Wise segregation of nuisance industries to certain districts or parts of a city is not, as a rule, a detriment but a talking point for a city. Such industries as produce odors, smoke, sludges, and objectionable by-products when segregated to certain districts leave other districts open for location of the less objectionable industries.

(12) COMPETITIVE, FEEDER, AND CONSUMER INDUSTRIES—It is important, on the one hand, to know what competition the proposed industry will have in its own territory, and, conversely, what feeder and consumer industries are at hand, the

first to supply the needed processed material for its special use and the second to purchase its products.

Relative Importance of Various Factors

In an analysis of industry we find that the order of importance of these twelve factors is often changed, so that in one case one factor may predominate and in the other another. It is to be noted, however, that distribution, favorable freight rates, markets, and labor conditions become paramount, in basic industries, after it has once been established that favorable fuel or power costs and, at least, competitive raw material costs are obtainable for that industry. That is, given favorable fuel and raw materials, then distribution, favorable freight rates, markets, and labor conditions are the next governing factors, as a rule, in the establishment of a basic industry. In the establishment of intermediate industries these same factors become paramount when it has been determined that these industries may obtain, under favorable conditions, those finished products which are their chief raw materials. For tributary industries these same four factors are the chief governing factors without any modifying conditions.

Industrial Measurements

I—Weighing[1]

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Gifted foremen used to be able to squint one eye and estimate the amounts of materials going into a batch. Either the trait is dying out and foremen aren't what they used to be, or else the old-time experts were really somewhat less accurate than the legends assert. At any rate, modern technology is no longer content with approximations in measurement. This article describes the developments which have been taking place in the weighing of solid materials in industry, both by manual processes and automatically. Future articles will deal with other types of industrial measurements, such as determination of gas and liquid flow, gas composition, temperature, and hydrogen-ion concentration.

In treating the subject of industrial weighing it will be convenient to take the viewpoint of the application of the equipment, rather than to discuss specifically the mechanical features of all the types of scales available. Some mention will be made of these mechanical details, but no attempt will be made at a complete description of individual scales or at a complete comparison of different types. A simple division may be made, for the sake of clearness, into the weigh-beam and pendulum types of weighing devices. In the first type the weight of an object is transmitted by levers to a weigh-beam, which is balanced by varying either the position or the amount, or both position and amount of weights upon it, while in the second type the weight of the object is transmitted to a lever, which lifts a constant weight in a vertical arc against the force of gravity.

The first type of weighing mechanism may be operated manually, semi-automatically, or automatically. In manual operation the load is balanced by hand, and the weight is read and recorded by the operator. In semi-automatic operation the load is balanced mechanically, and the weight is indicated by the machine, but is read and recorded by the operator. In complete automatic operation the machine not only balances the load, but records the amount of the weight by printing on a slip of paper or by actuating the mechanism of a mechanical counter or a continuous recorder of the familiar circular type. The second type of weighing mechanism is almost universally used as a semi-automatic installation, the weight being indicated on a dial and read and recorded by the operator.

With this brief classification of the types of industrial scales for an introduction, attention will now be directed to the weighing problems occurring in manufacturing the products of the process industries. These problems, when reduced to their simplest terms, may be grouped under three heads: (1) weighing of raw materials; (2) compounding and check-weighing; (3) packaging and product measuring. Some typical applications of scales in each of these three fields will be discussed in the following sections.

Weighing of Raw Materials

No plant can afford to operate without an accurate check on the amounts of its raw materials, whether they are supplied in cargo, carload, or truck lots. Certain mechanical weighing devices are particularly well adapted to this type of service. Hopper scales and conveyor scales will handle a continuous flow of material from transportation to storage, or from storage to process, while scales of the platform type are built in models to weigh batch lots ranging from a loaded freight car down to a wheelbarrowful.

The hopper scales adapted for weighing-in raw materials reverse the ordinary process of weighing, since they measure and pass loads of material against a predetermined standard. The weighing hopper is mounted on one end of a lever, which carried at the other end a variable counterbalance which can be adjusted and locked at the point necessary to give a certain weight discharge from the hopper. As the hopper fills with material to the desired weight, it starts to drop. The movement of the lever arms actuates the feed shutoff, while further travel opens the hopper discharge. Relieved of its load, the hopper moves upward again, closing its own discharge gate and opening the feed-gate again. An automatic counter records the number of cycles, and this value multiplied by the standardized weight of a single discharge gives the total weight of material passed through the hopper. Hopper scales are much used on dry materials which will not ball up and cling to the hopper. Some of their applications are the handling of coal, of grain to elevator storage, and of such raw materials as crushed limestone or sugar beets from storage to process.

Conveyor scales differ fundamentally from scales weighing a dead load in that they must integrate the instantaneous weight of the material on a section of conveyor belt against the rate of belt travel. This problem of mechanical integration has produced several ingenious devices. The most recent of these is the electrically operated system of the Telepoise. A short section of the conveyor is suspended from weighing levers working against precision springs. The levers and springs control the position of a contactor,

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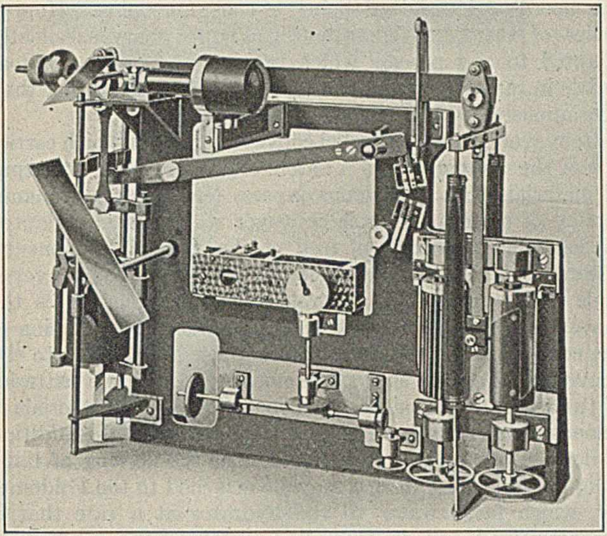
[1] Received March 15, 1929.

described below, which is connected to a registering device placed at any distance, and to a graphic recorder which shows the flow of material on the conveyor, including all variations and interruptions.

The contactor mechanism of the Telepoise is shown in Figure 1. The small vertical drums at the lower right revolve toward each other, and are driven directly by chains and gearing from a traction roller riding on the inside of the return span of the conveyor belt. The left-hand drum has a ridged surface, the separate ridges acting as cams to push a contactor suspended from the weigh-beam against the right-hand drum. The latter has a surface half of which is electrically conducting and half non-conducting, the line between the two portions following a true helix. With the belt running, the contactor is pushed periodically several times a second against the right-hand drum by the revolution of the ridged left-hand drum. When there is no load on the belt, the contactor hangs at its lowest point, where it does not touch any of the electrically conductive surface of the right-hand drum. With a load on the belt the contactor is pulled up between the drums, its position being determined by the weight on the belt. The contacts with the conducting portion of the right-hand drum allow the passage of electric current impulses to the register and recorder. Increased weight on the belt raises the contactor, resulting in an increased number of transmitted impulses per unit of time, while decreased weight on the belt lowers the contactor, cutting down the number of transmitted impulses. Similarly, increased belt speed increases the number of contacts per unit of time, because the rate of rotation of the drums is proportional to the rate of belt travel. The number of electrical impulses to the register is therefore a combined measure of the rate of belt travel and of the weight of material on the belt.



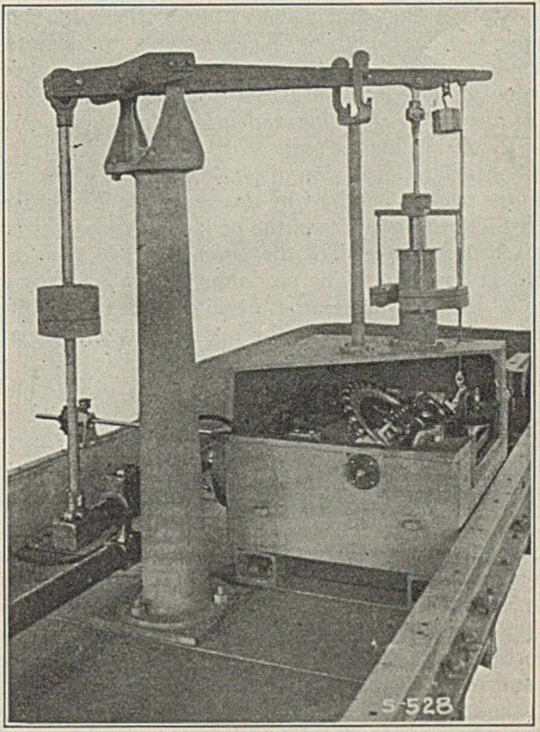
Courtesy of John Chatillon & Sons

Figure 1—Integrating Mechanism of Telepoise Conveyor Scale

Integration of weight of material on belt against rate of belt travel is accomplished electrically by means of contactor suspended from weigh-beam between revolving drums one of which has a variable contact surface.

The Telepoise can be balanced directly by means of a test weight by merely shifting a lever, which automatically cuts out the recording mechanism and shows by an ingenious arrangement of moving pointer and dial whether the scale is in accurate balance. Another feature is a percentage load indicator consisting of a mirror system so arranged that the movement of the weigh-beam reflects a black line on a large illuminated ground glass calibrated in per cent of full load. This ground glass is set so that it may be observed by the operator controlling the feed of material to the belt.

Another clever integrating device for belt conveyor weighing is included in the Conveyor Weightometer, the essentials of which are shown in Figure 2. An aluminum disk with small bakelite rollers mounted around its circumference is suspended on a frame so that it can rotate freely and at the same time swing freely on ball bearings between a horizontal and a vertical position. A continuous small belt driven from a traction roller on the belt conveyor is pressed against opposite sides of the aluminum disk by small pulleys. When the disk is vertical, as it is when the conveyor is running empty, the component of the motion of the small continuous belt tending to rotate the disk is zero. When the conveyor is loaded, however, the weight transmitted through the lever systems from the weighing rollers under a section of the conveyor swings the disk from the vertical toward the horizontal position to a degree proportional to the load on the conveyor. In such a position the movement of the small continuous belt exerts a rotating action on the disk, and the rotation of the disk is recorded on a continuous counter. The more nearly the disk approaches the horizontal the greater becomes the component of the motion of the small continuous belt in the direction of rotation of the disk. Since the rate of travel of the small continuous belt is directly proportional to the rate of travel of the conveyor belt, and since the angle of the rotating disk is proportional to the instantaneous weight on the weighing section of the belt, the resultant rate of rotation of the disk is a measure of the rate at which material is being conveyed.



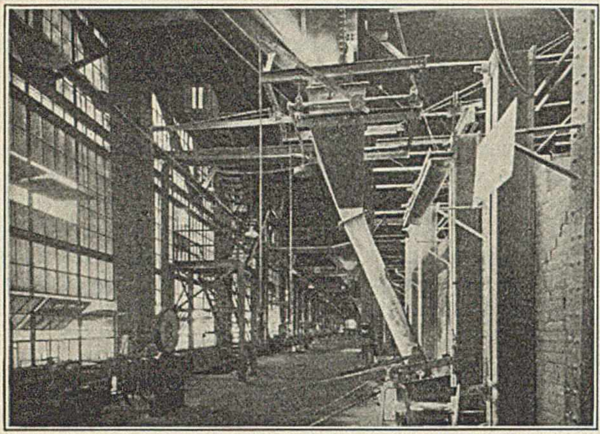
Courtesy of Merrick Scale Mfg. Co.

Figure 2—Integrating Mechanism of Conveyor Weightometer

Cut-away view shows mechanical integrating device described in text.

The Conveyor Weightometer weigh beam is counterbalanced by a cylindrical steel float partially immersed in a bath of mercury. Calibration is accomplished by suspending a test section of roller chain of known weight on the weighing section of the conveyor while the conveyor is running at normal speed. This simulates a constant known load. Adjustment for the weight of the empty belt is made with the conveyor running unloaded.

Platform scales of the automatic type are applicable to the handling of a continuous flow of material contained in small plant trucks, narrow-gage rail buggies, or carriers on overhead monorail lines, the platform in the last case being replaced by a weighing section of the rail mounted on levers connected to the scale mechanism. The automatic weighing and recording is carried out by mechanisms such as the Mechanical Weighman, which utilizes the disk-and-belt principle of the Conveyor Weightometer to operate the balancing weight on a weigh-beam, and automatically records the value of each load on a totalizing counter. The same type of automatic weighing and recording mechanism may also be applied to hopper scales.



Courtesy of Toledo Scale Company

Figure 3—Hopper Scales Measuring Feed of Batch to Glass Furnace

Flow of batch into weighing hopper is registered on dial scale on operating floor to left of picture.

Semi-automatic operation of platform scales of the weigh-beam type may be obtained by the use of the Weightograph, a weight-indicating device of the pendulum type, which may be attached to the end of the weigh-beam to face in any convenient direction. The pendulum carries a weight scale, the numbers on which are transmitted to an illuminated ground glass easily read by the operator at a considerable distance.

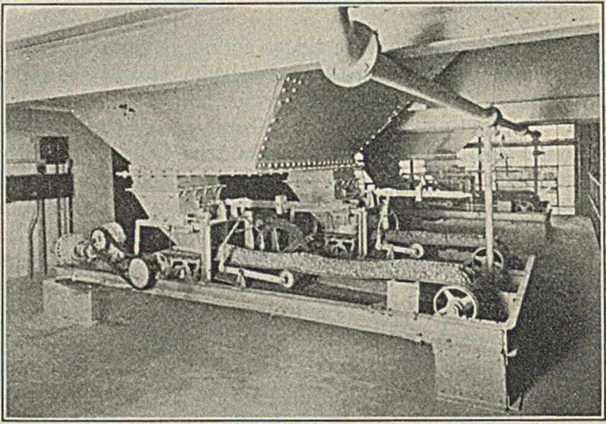
Manually operated platform scales are useful for handling infrequent loads of material, but are not good practice for large plants operating on a continuous schedule of raw material input.

Compounding and Batch Check-Weighing

For making up small batches of material, as in the compounding of rubber accelerators or of dough in bakeries, small platform scales are used with ungraduated dials showing a center indication and a warning range above and below the correct balance. For larger industrial operations platform and rail scales find varied uses. In several large glass plants the components of the batch are weighed into a special truck running on a track below a line of storage bins, and the complete batch is then check-weighed on rail scales at the end of the run. These special batch trucks are merely containers mounted on platform scales, the whole arrangement being carried in turn on the truck base. Scales of the pendulum type with direct indication of weights on a large dial are used chiefly for this work. If it is desired to keep the composition of a batch secret from the truck operator, the scale dial may be left blank, and adjustable indicators supplied instead, these being fixed at the points on the dial corresponding to the desired weights of the various components of the batch.

Hopper scales are also used for measuring batches of material to processes. Figure 3 shows in the foreground one of a battery of hopper scales feeding to glass furnaces. The operation of this type of hopper scale differs from that previously described for the weighing-in of raw materials, in that the amount of material taken into the hopper from the storage bin is indicated directly on the large dial on the operating floor, and this amount is directly controlled by the operator instead of being a constant value. Hopper scales of the type illustrated in Figure 3 are excellently adapted to any process which requires the feeding of materials in rather large quantities, but at intervals rather than continuously.

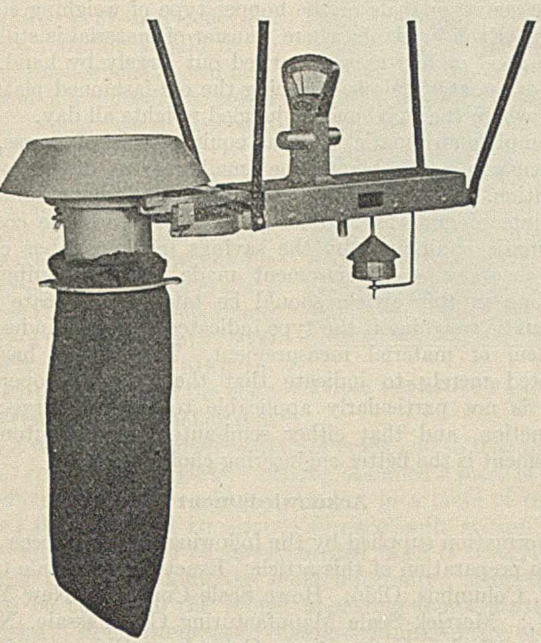
Conveyor scales on parallel conveyors, each of which carries one of the components of a batch, offer a check on the input of materials to a continuous process feed, as in the manufacture of cement. Simple conveyor scales are not adapted to controlling the rate of feed of the various components, however. The Poidometer goes a step beyond the conveyor scale and supplies this control. This equipment uses the movement of a series of lever arms, actuated by a section of the conveyor belt, to control the hopper gate feeding to the conveyor. Figure 4 shows poidometers arranged in batteries of two each for the purpose of proportioning raw materials in cement manufacture. For operations requiring the addition of definite proportions of water, such as the slaking of lime, a liquid-measuring device may be attached to the Poidometer, which feeds water to the hydrator at a rate that is predetermined and is controlled by the same mechanism which feeds the lime to the conveyor. Poidometers are particularly applicable to the control of compounding in any process where operation is continuous and dry granular materials are to be handled in large quantities. They are generally equipped with automatic controls which will stop all of the conveyor scales in a battery if any one fails to receive its proper amount of material. Another attachment is provided for batch work which will stop the conveyor scale after a predetermined amount of material has been delivered by it. The amount of material carried is calculated from the setting of the scale weights on the weigh-beam and the distance traveled by the belt, as recorded on a continuous counter.



Courtesy of Schaffer Poidometer Company

Figure 4—Poidometers Proportioning Materials in Phoenix Portland Cement Company Plant

Installations are in operation with as many as sixteen of these feeder conveyors operating in parallel for the compounding of a mixture. They are in use for the extensive handling of material in the clay products, gypsum, lime, fertilizer, cement, and similar industries, and for handling grain, as well as coal and ashes in power plants. The guaranteed accuracy for normal operating conditions is 99 per cent.



Courtesy of The Exact Weight Scale Co.

Figure 5—Fertilizer Sacking Scale

Packaging and Product Measuring

The estimation of the amount of a product from the weighing of the raw materials entering into its manufacture allows too many loopholes for loss in processing to be tolerated by careful engineering executives. The product, not only of the final process of a plant, but also of the different stages in processing, should be checked to make possible the reduction of manufacturing losses to a minimum.

In all of this weighing of intermediate and final products the conveyor scale is important for the plant in which production is arranged on a continuous interlocking basis, and the materials are such as can be handled well in conveyors of the belt, bucket, or pan type. Where plants are built for batch operation, the platform scale for the weighing of hand trucks or buggies, or for adaptation to a simple roller conveyor, is likely to be favored. The hopper scale may also be used at the end of a continuous conveyor as a measuring unit discharging to storage or loading material for transportation.

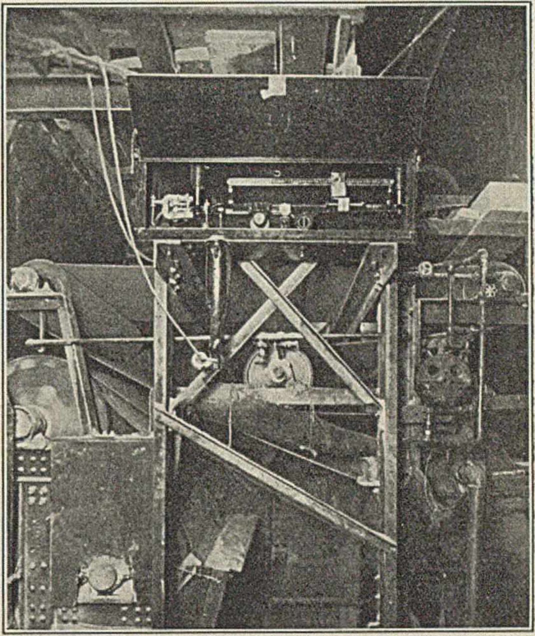
For products distributed in packages, rather than in carload or cargo lots, there are numerous types of scales adapted for special conditions, such as sacking scales, and package check-weighing scales or difference weighers. Sacking scales are of two types. The first is an ordinary platform scale, the feed hopper being arranged over the platform so that the sack when attached to it rests upon the platform. The other type of sacking scale is illustrated in Figure 5, the bag being suspended from a feed hopper which is supported by the lever mechanism of the scale. Such scales are used largely for sacking fertilizer, grain, flour, cement, plaster, salt, and similar materials.

Where products are put up in small cartons by automatic filling machinery, a checking scale is necessary to insure against a continued run of underweight or overweight packages. Check-weighing is usually done by hand, sample packages being taken at intervals from the line leaving the filling machine and rapidly compared with the standard package weight on equal-arm balances with scales graduated to show a certain small range of underweight and overweight. Here the amount of deviation from the desired constant value is the important thing rather than the actual total weight, so that scales of this type are frequently called difference weighers. A typical application outside of the field of packaging is the checking of rubber heels before vulcanizing. Overweight is trimmed off, the rubber scrap being returned together with underweight heels to be re-used.

Counting scales have an important place in industries manufacturing a small uniform product, such as washers, fuller balls, special bolts and nuts, bushings, small molded articles, and similar small specialties which are sold by quantity. These counting scales are so constructed that one object in one pan will balance a certain number, as fifty or one hundred, in the other pan. They are frequently referred to as ratio scales for this reason.

Overhead monorail systems are used extensively in packing houses, textile mills, paper mills, and foundries for transferring products. Weighing sections in these monorail tracks connected to dial indicators allow the rapid determination of the weights of heavy articles in transit.

An interesting development from the ordinary conveyor scale is a machine developed for weighing continuously a sheet product such as auto-top material, paper, or rubber tire tread. The strip of material passes over a weighing roller connected to a lever system as in the conveyor scale, and records on a dial the weight of the moving material. Such scales give a constant check on the uniformity of the product. Figure 6 shows a typical installation and emphasizes the small amount of space required by the actual weighing mechanism. The weighing roller is the small-diameter roller in the center of the illustration, one end of which is supported in a bearing on the weigh-beam.



Courtesy of Toledo Scale Company

Figure 6—Continuous Scale Recording Weight and Checking Uniformity of Sheet Product at End of Manufacturing Process

Weighing roller at center of span between upper large rollers is suspended at one end on bearing supported by weigh-beam of scale.

Important Factors in Industrial Weighing

The chief requisites of an industrial weighing mechanism are accuracy, ruggedness, speed of weighing, and elimination of errors in reading. A very good degree of accuracy may be obtained with any of the types of scales mentioned; conversely, any of these types may become very inaccurate if not consistently checked. In general, the accuracy of most industrial installations should be not lower than 99 per cent. It is stated previously in this article that one type of conveyor scale is guaranteed to meet this standard, while a recent English article (*1*) claims that a good hopper type scale should be accurate to within 0.2 to 0.5 per cent.

Most industrial scales are constructed to stand punishment, but the engineering excellence is likely to vary directly with the price. Particular attention should be paid to the manner of suspending knife edges to eliminate scraping over the surfaces upon which they bear, and to the maintenance of constant belt tension in conveyor scale installations.

The factors of speed of weighing and elimination of errors in reading are closely related, and are not, as in the classic dilemma of efficiency and economy, mutually incompatible. Weighing by completely manual operation is the slowest method and the one which introduces the greatest number of opportunities for error. Semi-automatic weighing, in which the balancing is done automatically and the weight is merely read off by the operator, is a great improvement both in speed and in elimination of errors, but complete automatic weighing, in which the final step of recording the weight is also carried out by the machine, represents the most rapid and foolproof system of all. It is absolutely necessary, of course, that automatic weighing devices be checked frequently to detect possible errors of adjustment, but if this is done they provide an invaluable measuring instrument for the large-scale operation of industrial processes.

The trend in the United States at the present time is predominantly in favor of the automatic handling of processes, because it has been very definitely proved that a machine can always surpass a man at doing anything that has to be done repeatedly. The trend toward automatic equipment is reflected in the replacement of the hand truck by the continuous conveyor, a change which carries with it the replacement of the manually operated scale by the automatic conveyor scale or the hopper type of weighing equipment. Even in plants where transfer of material is still, for some good or bad reason, carried out largely by hand, the semi-automatic scale is replacing the old-fashioned platform scale where the weighmaster juggled weights all day.

Complete automatic weighing equipment is, of course, not particularly applicable to the small-scale or discontinuous operation. The process in question must involve sufficient amounts of material and labor to overbalance the cost of automatic equipment by the savings in time, labor costs, and accuracy of measurement made by the equipment. Nothing in this article should be taken to indicate that automatic weighing is the type indicated for every industrial problem of material measurement. This article has attempted merely to indicate that the manually operated scale is not particularly applicable to modern large-scale production, and that either semi-automatic or automatic equipment is the better engineering choice.

Acknowledgment

Information supplied by the following firms has been used in the preparation of this article: Exact Weight Scale Company, Columbus, Ohio; Howe Scale Company, New York, N. Y.; Merrick Scale Manufacturing Co., Passaic, N. J.; Ralston Scales Corporation, Columbus, Ohio; Schaffer Poidometer Company, Pittsburgh, Pa.; Toledo Scale Company, Toledo, Ohio; E. J. White, Sales Agent, Telepoise Conveyor Scale, New York, N. Y.

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(1) Benton, *Chemistry Industry*, **46**, 741, 764 (1927).

Making the Glass Disk for a 70-Inch Telescope Reflector[1,2]

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Details are given of the procedure followed in making a glass disk 70 inches in diameter and 11 inches thick for use as a reflector in an astronomical telescope. These include the making of the pots, the modifications in the construction of the melting furnace, the construction of the mold and annealing furnace, the methods of measuring and controlling temperatures, the melting and casting of the glass, essential data on annealing the glass, the determination of the quality of annealing (the amount and distribution of the residual strain), and the drilling of the hole to accommodate a Cassegrainian mounting.

The manufacture of glass for ordinary optical instruments is a well-established but limited industry, there being probably not more than ten optical glass plants in the world. This industry is, however, very necessary for the maintenance and development of our commercial and scientific enterprises, since a lack of suitable glass for making microscopes, cameras, surveying instruments, range finders, etc., would greatly hamper all work in which such instruments are used.

Difficulties which are of minor importance in making glass for smaller optical instruments become more serious as the size of the instrument, and consequently the size of the glass, is increased. The most serious difficulties met in producing large pieces of glass include properly melting the amount of glass required, transferring it to a mold to produce the desired shape while maintaining the necessary quality, and finally cooling it at rates such that it does not crack and that it will be well annealed (free from disturbing internal stresses).

The proper cooling (annealing) of large pieces of glass is probably the most exacting and tedious phase of the work, and this cannot be successfully accomplished without knowing the thermal properties of the glass and adequately controlling the temperatures of the annealing furnace.

Plan of the Work

Because of the lack of definite information on methods of making satisfactory pieces of glass which could be used

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[1] Received May 21, 1929.

[2] Publication approved by the director of the Bureau of Standards of the U. S. Department of Commerce.

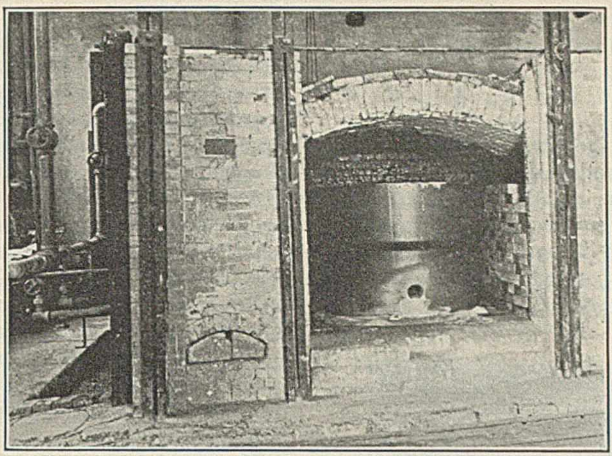

Figure 1—Melting Furnace (Front Removed) and Pot after the Glass Had Been Made

for large telescope reflectors, the Bureau of Standards became interested in the problem and undertook to make the glass for a 61-inch reflector. Such a reflector should be 10 inches thick when finished and, if made of a borosilicate crown glass, would weigh approximately 2960 pounds.

It was decided to make the disk about 70 inches in diameter and 15 inches thick in order to make ample allowance for faulty edges. A piece of glass having these dimensions would weigh approximately 5000 pounds. The first plan involved the melting of the glass in one large pot and cooling it in such a way that the glass would not crack and so that the pot would spall from the glass. Having obtained a piece of glass of sufficient size, it would then be put in a mold of the required diameter and an electric furnace built around it so that the glass might be slowly heated until it became soft enough to flow and fill the mold uniformly; after this it would be cooled to the proper annealing temperature and annealed. Four attempts to obtain the initial piece of glass were unsuccessful because the glass cracked each time during cooling. This method was then discarded and a different one tried. In the new method the glass was to be melted in a pot provided with a hole near the bottom, this hole being stopped with a water-cooled metal plug. When the glass was properly melted, a metal trough was to be placed between the pot and mold, the plug removed, and the glass allowed to flow into the mold where it would be ready for cooling and annealing.

The successful application of this method depended on three major conditions: first, preventing the glass from leaking through the hole in the pot by means of a water-cooled metal plug; second, adequately controlling the flow of glass from the pot to the mold; and third, obtaining a satisfactory friable lining for the mold. The advantage of this over the first method tried was that only one cooling of a large and relatively thin slab would now be required, whereas the first one offered three additional hazards: first, the possibility of the glass cracking during the initial cooling on account of its great thickness; second, the possible failure of the pot to break away from the glass; third, the possibility of cracking the glass during reheating for softening in the mold.

The Pots

It was first necessary to make pots sufficiently large to hold the amount of glass required. The dimensions of the furnace available for the purpose determined, to a large extent, the actual dimensions of the pots, which had, after burning, a depth of 33.3 inches and an internal diameter of 47 inches at the top and 43 inches at the bottom. The pot walls were $3^{1}/_{2}$ inches and $4^{1}/_{2}$ inches thick at the top and bottom, respectively (see Figure 2 for a cross-section view of the pot). The pots were "cast" in a plaster of Paris mold by a method developed at this bureau (*3*) and used in making all of our glass pots, but since these large pots were more than six times the size of our ordinary melting pots, it was necessary to make a larger mold for casting them. The sides of the mold consisted of three vertical sections, the core of a monolithic hollow piece, and the base of a single solid slab. About 10 tons of plaster of Paris were used in making the forms, the model, and the finished mold. Each pot was made from 2500 pounds of domestic clays and feldspar blended in the following proportions:

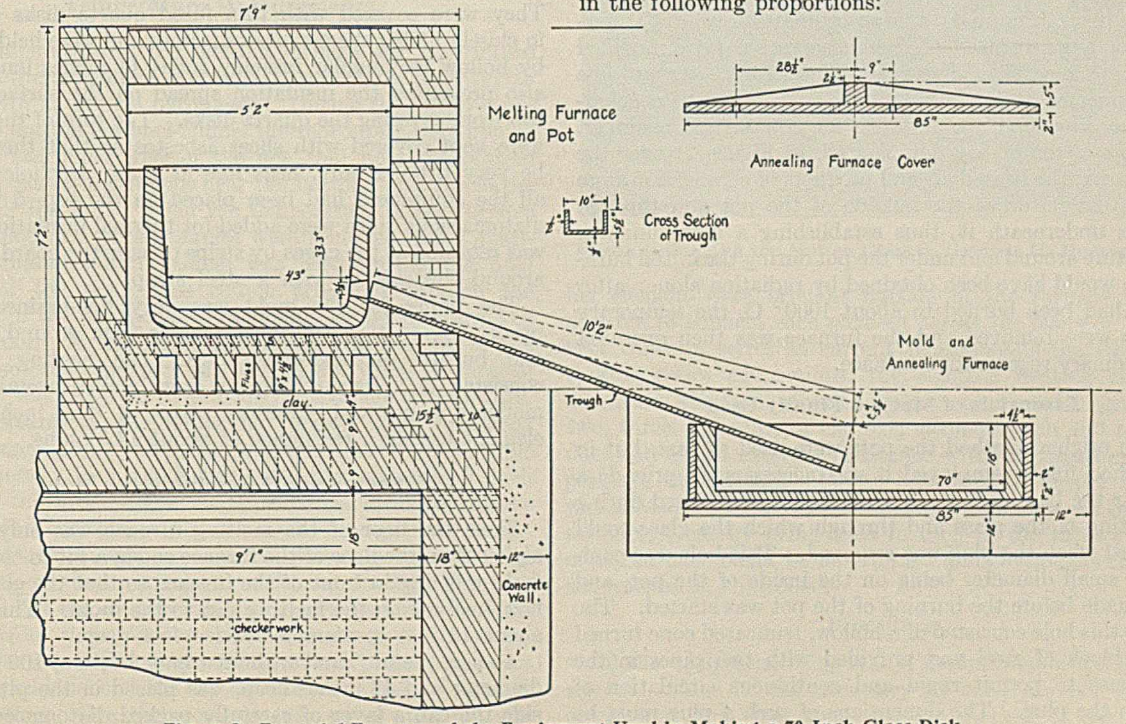

Figure 2—Essential Features of the Equipment Used in Making a 70-Inch Glass Disk

	Per cent
Feldspar	8
Tennessee ball clay	30
Kentucky ball clay	21
North Carolina kaolin	23
Delaware kaolin	9
Georgia kaolin	9

The clays were thoroughly blunged with water to which 0.6 per cent of water glass was added and the resulting slip was poured into the mold. After standing in the mold for 2 days, the core was withdrawn and the next day the sides of the mold were removed. The pot was then slowly dried until most of the water had evaporated; finally it was air-dried for 6 months before being used (*2*).

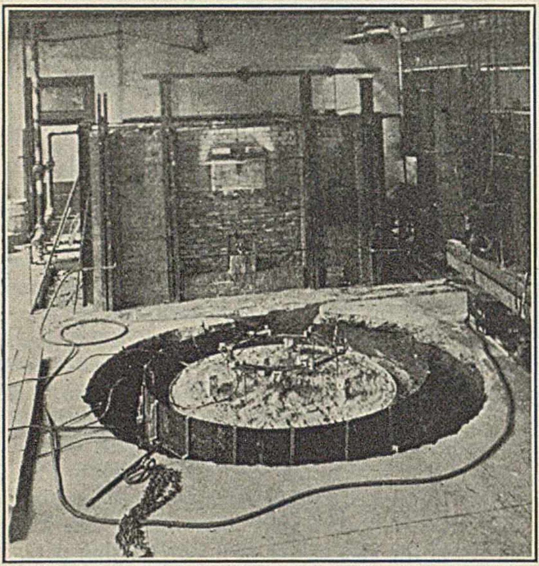

Figure 3—Melting Furnace (Back), Assembled Mold and Annealing Furnace (Center), and Trough (Right)

This picture was taken just before the lid was removed preparatory to casting the glass.

Melting Furnace

The furnace (Figure 1) was an ordinary down-draft, gas-fired, single-pot furnace of the regenerative type modified by building a series of flues in the floor, each alternate flue being connected at one end with the space over the checkerwork, the other end opening into the combustion chamber. By means of temporary dampers (*S*, in Figure 2) over the checkerwork, the heated air and products of combustion were forced to travel down the outside of the pot and through the flues underneath it, thus establishing a more uniform temperature around and under the pot during the initial burning than would have been obtained by radiation alone; after the pot had been burned to about 1000° C. the temporary dampers were removed and the furnace was then operated as an ordinary regenerative furnace.

Essentials of Method Finally Used

In the original method the pots were used as cast, but in the method finally employed it was necessary to provide a hole near the base of the pot which could be plugged during the melting of the glass and through which the glass could be tapped when the plug was removed. This hole was conical, the small diameter being on the inside of the pot, and it was made before the burning of the pot was started. The plug for this hole consisted of a hollow, truncated cone turned from a block of steel and provided with two pipes in the larger base to permit rapid and continuous circulation of water in the plug. The dimensions of such a plug must be based on the dimensions of the hole after the pot is burned, but since the shrinkage of the pot body from air-dried to burned condition was known to be about 8.5 per cent, the dimensions of the plug required could be predicted fairly accurately from those of the hole before burning. Furthermore, it is not essential that the dimensions of the hole and plug should be the same, but the tapers of both should be practically the same, and the small diameter of the plug should be such that the plug, when firmly seated in the hole, could not reach beyond the inner surface of the pot. In this particular case the hole in the pot was made about 5 inches in diameter at the large end and had a taper of about 8$^1/_2$ degrees. The plug was about 3$^3/_4$ inches long.

The combined mold and annealing furnace (Figure 2) into which the glass was tapped consisted of four essential parts: the metal forms, the lining, the heating elements, and the insulation.

The metal forms were made of cast iron and consisted of a top, a ring, and a base. The top, which was 85 inches in diameter and 2 inches thick, was flat on the lower surface and had six radial ribs on the upper surface; these ribs were joined at the center of the upper surface in a cylinder 5 inches high and 5 inches in diameter and tapered to the surface of the top at its edge (Figure 2). The ring was 79 inches in inside diameter, 2 inches thick, and 19 inches high. The base was the same as the top except that it was not ribbed. The base, ring, and top were drilled and tapped for eyebolts to facilitate handling.

Six equidistant holes, $^1/_4$ inch in diameter and approximately 2 inches deep, were drilled in the edges of both the base plate and the top. Six similar holes were drilled into the ring half way between its top and bottom. These holes were all for thermocouple installations. In each rib about 20 inches from the center of the top a $^1/_4$-inch hole was also drilled, two being used for thermocouples and the other four to accommodate supports for the frame carrying one of the power lines. Six 2-inch holes were drilled through the top between the ribs, three of these being 9 inches from the center and in alternate segments, the other three being 28$^1/_2$ inches from the center and in the remaining three segments. These were to permit local inspection of the glass during the cooling. They were covered with thin fused quartz disks mounted in closely fitting sheet-asbestos frames and were held in place by hollow rectangular fire-clay tubes 14 inches long, which also prevented the insulation spread on the surface of the top from covering the quartz disks. The tops of these tubes were kept covered with sheet asbestos so that there would be very little, if any, heat loss at these peepholes. After all the equipment had been placed on the top, 5 inches of diatomaceous silica were added for thermal insulation. This was retained at the edges by strips of asbestos board fastened around the casting with a steel strap.

The lining for the mold was very fine-grained friable brick (2$^1/_4$ × 4$^1/_2$ × 9 inches) made from ground, bonded, and burned diatomaceous silica. The heating elements consisted of spirals of No. 16 gage nickel-chromium wire mounted in grooved refractory plates (9 × 14 inches), each element having a resistance of about 13.5 ohms.

Placing and Assembling the Mold

Since the floor of the melting furnace was only slightly higher than the floor of the furnace room, a pit to contain the mold was dug in front of the furnace so that the glass might flow freely from the melting pot to the mold. This pit was about 15 feet in diameter and 4 feet deep.

A sheet metal "can" without top or bottom, 109 inches in diameter and 48 inches deep, was placed in the pit, and inside the can a layer of carefully packed diatomaceous silica

1 foot thick was placed on the ground. Eighteen heating elements were so placed on the insulation that they would be symmetrically arranged under the base plate and be so distributed that each element would heat approximately an equal area of the base plate. The leads from each element were ultimately connected to the power line after bringing them through holes previously drilled in the can at the proper level. The base plate was put in position over the heating elements and the ring put in place concentrically with respect to the plate. Eighteen heating elements were fastened around the outside of the ring and the leads from each one of these elements were also carried out through small holes in the can. The space between the ring and the can was then filled with powdered insulation which was not packed.

The bricks for the bottom of the mold were laid without mortar and in the herring-bone style on the $4^1/_2 \times 9$ inch face, care being taken to have the bricks very well fitted and to keep the upper surface level. After the entire base was covered in this manner, the sides were laid up to give a wall 15 inches high and $4^1/_2$ inches thick. Each brick in the wall was so cut at the ends that the wall conformed nearly to the curvature of the ring. The top of the furnace was provided with eighteen heating elements placed similarly to those under the bottom, the leads from each plate being brought up to a wooden framework supported about 18 inches above the casting by rods fitted into the holes drilled in the ribs of the casting (Figure 3).

The channel which was used for conveying the glass from the pot to the mold was 5 inches deep, 10 inches wide, and 10 feet 2 inches long. It was made by cutting off both flanges from one side of a standard 10-inch H-beam (55 pounds per foot). It was very carefully sand-blasted to remove all traces of rust and scale so that the glass might flow without being contaminated with iron oxide and without the possibility of scale snapping off as the metal became heated. The channel was supported near both ends from an overhead crane with flexible steel cable over pulleys in such a way that the elevation of either end could be controlled independently.

Temperature Measurements

The temperature of the melting furnace was determined both with thermocouples connected to a portable potentiometer and with an optical pyrometer. During the initial burning of the pot ten chromel-alumel thermocouples were used—four near the upper edge of the pot, four near the bottom (outside), one inside the pot near the bottom, and one in the sand under the pot. When the temperature of the furnace reached 1000° C., these couples were removed and a platinum platinum-rhodium couple was used during the final burning of the pot. This couple projected through the back wall of the furnace and was about 18 inches above the furnace floor. It was also used during the melting of the glass to indicate constancy of temperature while the optical pyrometer was relied on to indicate the average temperature.

Temperatures of the annealing furnace were measured with chromel-alumel thermocouples connected to a portable potentiometer. The installation of the thermocouples in each section of the furnace was made before the insulation above the base plate was put in place. In order to prevent breakage of the thermocouple protection tubes by a possible settling of the furnace, they were not brought out through the sides of the can, but the couples and tubes were made long enough to reach from their positions in the castings to the upper edge of the can. The thermocouples and protection tubes in the ribs and sides of the top extended straight up through the insulation. One thermocouple whose hot junction was about $^1/_4$ inch below the upper surface of a brick in the base of the mold and about 15 inches from the ring was brought out between the ring and the base and carried up to the edge of the can. In this case two tubes were used, one for each wire, because it has been found that protection tubes not closed at the inner end and extending through insulating material are liable to collect a small amount of water in the cold end and produce erratic readings; but if two tubes are used there is no reason to believe that collected water in either or both affects the readings. All couples were connected with a switchboard by means of compensating or extension lead wires and proper cold junction corrections were made. The cold junction for this work was in a pipe driven about 12 feet into the ground where the temperature did not change more than 2° C. during the entire operation.

Although twenty-two couples were installed, it soon became evident that it was not necessary to use more than five of them, because the temperature of the furnace was sufficiently well indicated by these five. However, occasional checks were made on all couples, using an independent short connection to the potentiometer.

Heating Current Installation

Arrangements were made to supply, if necessary, a maximum of about 50 kilowatts to the annealing furnace in case the preheating of the furnace and the heat from the molten glass did not bring the furnace temperature well above 600° C. From the main switchboard three lines were run to the furnace. Two of them were placed around the can, one at about the elevation of the base plate and the other opposite the middle of the ring. The third extended to the framework above the top of the furnace. Since the leads from each heating element were brought outside of the furnace, it was possible to connect each element across the leads or to connect them in series as current requirements dictated. By making series connections, the eighteen heating elements on each of the three circuits could be connected in groups of two, three, six, nine, or eighteen elements each and thus reduce the use of external resistance without disturbing temperature distribution. Power consumption of the furnace was measured with ammeters and voltmeters so that the amount of energy being used in each of the three sections of the furnace could be determined and, by means of external resistance, controlled.

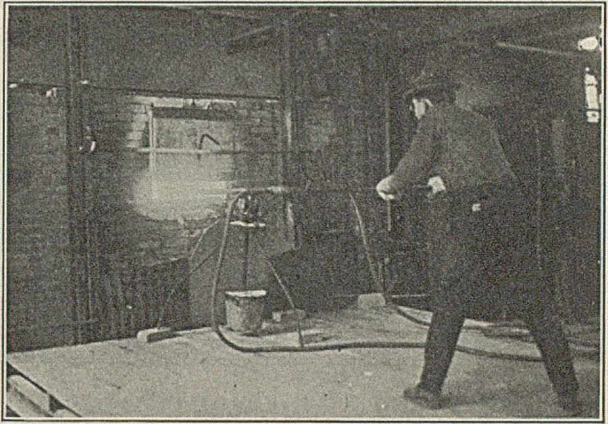

Figure 4—Stirring the Molten Glass to Increase Its Homogeneity

Procedure

All the equipment being ready, the burning of the pot was started. Since it was necessary to burn the pot without cracking it and since there was no method of adequately examining it after burning, it was burned very slowly, 30 days being required to reach a temperature of 1425° C. at which the glass would be melted. After the pot was properly burned at this temperature, the lower door in the furnace was opened, the water-cooled plug was fastened in place, and 1000 pounds of cullet were put into the pot. This was sufficient to fill the pot to a point above the hole and plug, and, since no leak was evident, the filling of the batch at the rate of 170 pounds per hour was started. The batch had the following composition:

	Per cent		*Per cent*
Sand	49.9	Barium carbonate	1.9
Boric acid	4.3	Potassium nitrate	6.5
Borax	17.5	Zinc oxide	1.9
Soda ash	5.7	Arsenic oxide	0.3
Potash (83 per cent)	12.0		

Approximately 5000 pounds of batch were used, requiring 31 hours to fill the pot. The temperature of the melting furnace was then reduced to 1400° C. and the stirring of the glass was started. This was done by hand, using a water-cooled iron stirring rod, and was continued for 6 hours. The stirring was then stopped and the temperature of the furnace reduced to 1350° C. While the batch was being filled and the glass was being stirred, current was applied to the annealing furnaces to heat and to hold it at about 400° C.

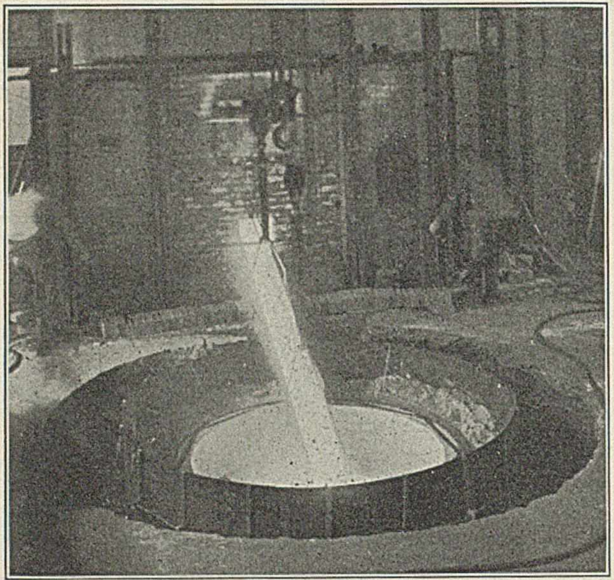

Figure 5—Initial Flow of Molten Glass from Pot to Mold

Figure 4 gives some idea as to the equipment used during stirring. The water-cooled stirring rod projecting into the furnace can be seen, and also the temporary flooring, placed over the mold, which was necessary to provide access to the furnace from the front. The time which elapsed between the end of the stirring and the actual tapping of the glass was greater than it should have been because, after the stirring was stopped, it was necessary to remove the flooring, the rails on which it was supported, and the lid of the mold, and to swing the channel into place. If this work were repeated, it would be more desirable to tap the pot from the side of the furnace opposite to that used for filling and stirring so that the stirring might be continued until the glass was being tapped. By so doing the prospects of getting glass relatively free from cords would be improved.

Casting and Annealing the Glass

When all arrangements were completed for tapping the pot, the supports for the water-cooled plug were released and the plug removed. The glass in contact with this plug was practically solid and the molten glass did not begin to flow from the pot until the plug of cold glass became soft enough to yield. It then flowed very rapidly. As its level in the mold rose, the ends of the channel were adjusted so that one end remained practically fixed at the hole in the pot and the other was not permitted to touch the glass in the mold (Figure 5). When practically all the glass was in the mold, the trough was removed and the lid was put in place as quickly as possible to conserve a maximum amount of heat furnished by the glass. This was not a good procedure, because shortly after placing the lid on the mold it cracked in two places on account of too rapid heating, but fortunately this produced no undesirable results.

The maximum temperatures ever indicated by the thermocouples were about 850° C. in a rib of the lid, and about 1000° C. immediately below the surface of the brick in the bottom of the mold. At this time there were only the original 5 inches of insulating material on the top, but 24 hours later about 3 inches more of insulation were added. Nine hours later additional insulation was added until all metal parts of the mold were covered to a depth of 12 inches. The heat loss was then so slow and the amount of heat to be lost by the glass before reaching 600° C. was still so large that it was not necessary to use heating current for about 4 days, at which time it was applied intermittently to equalize the temperature of the system.

Since borosilicate crown glass of the composition used in this work can be cooled safely to 600° C. without danger of breaking, it was cooled to this temperature as rapidly as the furnace construction would permit, but without allowing any part of the furnace to cool below 600° C. Eight days after casting the glass the average temperature of the furnace was 596.7° C. Three days later the average temperature was 594.8° C. In the meantime the power supplied to the heating elements was 2752 watts. During the next 2 months the heating current was gradually reduced until the temperature for annealing (461° C.) was reached.

This temperature was based on the data of Adams and Williamson (*1*), who have shown that glass can be most efficiently annealed if the annealing temperature and subsequent cooling rates are properly chosen. Although the time required for stresses or strain in glass to disappear at temperatures just below the initial softening point of the glass is very short—say 2 minutes—it increases rapidly as the annealing temperature is lowered. However, the authors cited demonstrate that glass can be cooled more rapidly after annealing at lower temperatures than after annealing at higher temperatures. Ultimately, then, the time required for the whole operation (annealing and cooling) may be shortened if lower annealing temperatures and faster cooling rates are used. The most desirable annealing temperature for a piece of glass of any thickness can be computed from the following equations:

$$\log A = M_1\Theta_0 - M_2, \quad A = \frac{0.047}{C}, \quad C = 4.6\ Ba^2$$

in which Θ_0 is the desired annealing temperature (degrees Centigrade), a is half the thickness of the glass (in centimeters), and M_1, M_2, and B are constants whose values for borosilicate crown glass are 0.03, 18.68, and 2.85 $(10)^{-7}$, respectively. The time, t, in minutes, required for annealing or release of stress is found from $t = 0.37/A$. The initial

Note—In this presentation A may be called the "annealing constant" and depends on the rate at which glass anneals when held at constant temperatures. M_1 and M_2 are constants obtained by plotting $\log A\ (10)^5$ against temperature. B is a function of the birefringence produced by a given stress. In a paper of this kind a more comprehensive mathematical discussion would be out of place, and the reader is referred to the work previously cited for more detailed information.

cooling rate, h_0, after annealing is $5.2/C$ degrees Centigrade per minute, and the permissible cooling rate, h, at any temperature, Θ, below the annealing temperature, Θ_0, is obtained from

$$h = \frac{h_0}{2}(1 + 2^x), \text{ in which } x = \frac{\Theta_0 - \Theta}{20}$$

Since Adams and Williamson based their findings on pieces of glass much smaller than the piece being annealed, and since the validity of extrapolations from data obtained on small pieces to those for a much larger piece might be questionable, it was decided to anneal the glass about twice as long as computations indicated would be necessary and to cool it initially at about one-half the computed rate. The annealing temperature and cooling rates were based on a thickness of 31 cm., which was slightly greater than the actual thickness of the disk. It was felt that these safety factors would also offset the effect of any differences between the temperature of the glass and the metal castings in which the thermocouples were placed and of any inequalities in the temperature of the castings not indicated by the thermocouples.

The glass was annealed for 41 days at 461° C., the total power consumption during this time being 1890 watts distributed as follows: 660 watts on the bottom of the furnace, 444 on the ring, and 786 on the top. During the annealing period constant personal attention was given to the annealing furnace in order to adjust the heating current as frequently as might be made necessary by changes in the voltage of the power line. The care with which this was done is shown by the following: The average temperature of the furnace during the 41 days used in the annealing operation was 461.5° C.; the maximum average on any day was 463.4° C. and the minimum was 458.3° C.

Final Cooling

Assuming that the glass at the end of the annealing period was free from strain, it still was necessary to cool it so slowly that no great amount of strain would be present at the end of the operation. Although the data of Adams and Williamson indicated that an initial cooling rate of 2.33° C. per day and a maximum rate of 60° C. per day would be permissible, it was decided that the initial cooling rate used should be about 1° C. per day and the maximum rate should not exceed 10° C. per day; and if possible, this maximum would be restricted to 6° C. per day.

Cooling was first accomplished by reducing the power consumption 5 per cent of that required to maintain the constant annealing temperature and by applying this reduced amount of power until the temperature drop became definitely slower than it was at the beginning. Generally 5 days were required to show a definite decrease in the cooling rate. Sixteen similar cuts of 5 per cent each were made in the heating power, after which the amount of each cut was reduced to 2.5 per cent until the power used was only 5 per cent of that used for annealing. Finally cuts were made at the rate of 1 per cent. It was thought that the very slow cooling at lower temperatures was necessary because, in the final equalization of any unknown temperature differences in the system, temporary strains might develop in the glass which would be sufficient to break it, and this, of course, must be avoided if possible.

		TEMPERATURES AT DIFFERENT PARTS OF FURNACE					AV. TEMP.	GENERAL AV. TEMP.
		° C.	° C.	° C.	° C.	° C.	° C.	° C.
May 24	Top	610.5	611.7	611.7	612.8	...	611.7	611.7
	Ring	614.0	614.0	611.7	612.8	...	613.1	
	Base	610.5	610.5	608.1	608.1	614.0	610.2	
July 8	Top	465.7	466.4	466.4	...	...	466.2	466.7
	Ring	468.7	468.0	468.0	468.7	...	468.4	
	Base	466.4	466.4	465.3	465.3	463.4	465.4	
Nov. 19	Top	176.9	176.7	175.7	177.4	178.2	177.0	176.8
	Ring	177.2	176.9	176.9	177.2	...	177.1	
	Base	176.2	176.7	176.0	176.5	...	176.4	

The uniformity of temperature maintained during cooling is indicated by the preceding table.

Inspection during Cooling

When an attempt was made to project light through one of the peepholes in the top of the furnace and view the glass through another, it was found to be practically impossible because the lower surface of the quartz disks had been slightly etched by volatile materials such as alkali or boric oxides from the hot glass. After the disks were removed, resurfaced, and replaced, illumination and inspection of the glass through these peepholes were very easily accomplished, but the glass could only be examined in the relatively small parts immediately below the peepholes. However, a sufficiently good view could be obtained to justify the conclusion that the glass was still intact.

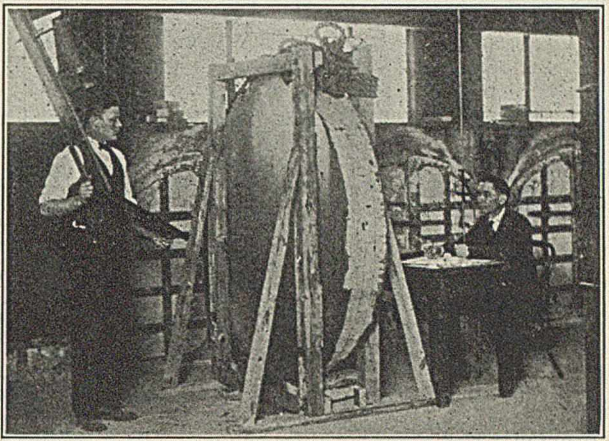

Figure 6—Examining the Glass for Strain

Four and a half months after the cooling from the annealing temperature started, the furnace and its contents were practically at room temperature. The surface insulation and the lid of the furnace were then removed and the glass was found to be in satisfactory condition. The disk was 69.75 inches in diameter, 11 inches thick, and weighed approximately 4000 pounds.

Quality of Annealing

The disk was removed from the mold and the bricks, which were superficially fused to the glass, were stripped off. This left the sides and bottom of the disk opaque because the glass had partially fused to the bricks. Before an examination for strain could be made it was necessary to grind the bottom of the disk with carborundum and water to remove the adherent particles of brick. The disk was then placed on edge in a wooden frame, and the ground surface coated with a heavy mineral oil, which rendered it sufficiently transparent to permit examination with polarized light. The magnitude of the residual strain was measured by examining small sections of the entire disk (Figure 6). The distribution or symmetry of strain was determined by projecting a divergent beam of polarized light against one surface of the disk and examining it through a Nicol prism from the opposite side. In this case the light source and observer were each about 30 feet from the disk and the entire disk was visible through the Nicol prism. The interference figure was very symmetrical with respect to the disk, intersecting exactly in its center, and the maximum strain detected produced a relative retardation equivalent to about 6 mμ per centimeter of thickness. This is well within the maximum strain permissible in optical glass used for optical instruments of highest precision.

Drilling the Hole

Large reflecting telescopes are generally equipped with one of three types of mountings—namely, the prime focus, Newtonian, and Cassegrainian. The last of these requires a hole in the center of the reflector so that light concentrated by the reflector may be returned by a secondary mirror to a point back of the reflector. This hole does not interfere with the use of the other mountings, but without it the Cassegrainian mounting could not be used. Hence it was decided to drill an 8-inch hole in the center of this disk, although several authorities said this could not be done without a very great possibility of breaking the disk. A possible cause of breakage during this operation lies in the fact that in cutting a hole the surface of the cut is very finely fractured; the fractures, being near the center of the disk and in the zone of high tensional stresses, may easily become the starting points of serious cracks if the glass is not sufficiently free from strain.

Figure 7—G. K. Burgess, Director of the Bureau of Standards (Right), and C. C. Crump, Professor of Astronomy at Ohio Wesleyan University, Examining the Disk after the Hole Had Been Cut. The "Core" Is Resting on the Surface of the Disk

The drilling was accomplished by attaching an 8-inch brass tube to a radial drill press and by slowly cutting out a core, using water and 150-mesh carborundum in the cut. About 70 working hours were required to cut this hole (Figure 7). It might have been done in much less time but, by working slowly, a partial adjustment of the glass to unbalanced stresses could take place and the possibilities of excessive local heating would be reduced.

This operation was conducted without any apprehension of possible cracking of the glass, although precautions were taken to protect the optician working on it in case the glass did "explode." These precautions consisted of bedding the glass on sand and surrounding it entirely with sand contained in the cast-iron ring used in the mold. The top was covered with 2 × 12 inch planks and $^1/_2$-inch sheet steel except for the hole through which the cutter passed.

Conclusion

Although the manufacture of large disks of glass to be used for reflectors in astronomical telescopes is ordinarily considered a difficult undertaking, it seems from the foregoing discussion that such is not the case provided sufficient time is taken to anneal and cool the glass properly.

Based on the results obtained in the work just reported, it seems quite possible that American manufacturers can easily go into this field of endeavor, if occasion presents itself, with reasonable assurance that their efforts will be successful and that they need not spend much, if any, time and money in developing a satisfactory method of operation.

Literature Cited

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Corrosiveness of Soils with Respect to Iron and Steel[1,2]

Preliminary Studies

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While corrosion is so widespread that it may be classified as one of our natural phenomena, it may also be considered first in magnitude among destructive electrochemical processes of industrial importance. The corrosion of pipe lines and other underground metallic structures represents a large proportion of the total corrosion waste in the world, the loss amounting to many millions of dollars annually. Most of the previous studies on the subject have been concerned with the kinds of material and their resistance to corrosion in various media, principally liquids and gases. In the present case, however, attention is directed to the medium—namely, the soil.

As an outgrowth of its work on stray-current electrolysis, the Bureau of Standards in 1922 began an extended investigation of the corrosive effect of typical soils in the United States upon ordinary commercial pipe materials. At that time over seven thousand weighed specimens of ferrous pipe materials were buried in forty-seven soils, which were selected with the coöperation of the Bureau of Soils. An aliquot portion of these specimens was removed every two years. Both the loss of weight and the depth of pitting have been determined for the 2-year, 4-year, and 6-year periods. The details of this work have been published (*3*).

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[1] Received March 28, 1929. Presented before the Division of Industrial and Engineering Chemistry at the 77th Meeting of the American Chemical Society, Columbus, Ohio, April 29 to May 3, 1929.

[2] Publication approved by the director of the Bureau of Standards of the U. S. Department of Commerce.

[3] Research associate for the Cast Iron Pipe Research Association.

Although this investigation is far from complete, the results to date show that the corrosion losses vary to a much greater extent among different soils than among different pipe materials. Both the loss of weight and the nature of the pitting are characteristic of the soil. Thus, specimens taken from a given soil are similar in appearance and depth of pitting irrespective of the kind of ferrous material.

The problem of mitigating soil corrosion is one for the metallurgist to solve by producing a material superior to those now economically available or for the chemist to solve by devising means of protecting the present commercial pipe materials. In considering the laying of a pipe line and its protection against corrosion, the desirability of knowing in advance the corrosiveness of the soil is apparent because it is important to know where protection is needed as well as where it is not needed. One of the present sources of economic waste is the expense of protective measures where they are unnecessary. It is therefore important to have methods of identifying non-corrosive soils as well as corrosive ones.

A method of studying soil corrosion based on the relation of salt content, acidity, and corrosiveness of soil to rainfall is suggested. The corrosiveness of soils as indicated by the initial losses of buried specimens in humid areas of the United States has been correlated with their acidity.

The total acidity of soils may be estimated by titration using the hydrogen electrode; and also by comparing the pH value of the soil in water and in a potassium chloride solution. A relation exists between the ability of a soil to react on iron with liberation of hydrogen and its total acidity as indicated by titration.

The corrosiveness of a soil in humid regions may possibly be indicated by its total acidity or by its action on iron with evolution of hydrogen.

Galvanic currents which accompany corrosion have been observed along a pipe line, far away from any source of electric power, by Logan (*4*) and others under conditions which indicate that such currents are due to differences in the character of the soils in contact with the pipe. The current on the pipe at some points along the line was in the neighborhood of an ampere. Along some portions of the line the current was found to be flowing from the soil to the pipe, while along adjoining portions, perhaps several hundred feet away, the current flowed away from the pipe. Thus, cathodic portions alternated with anodic portions and the corrosion seemed to be more serious over the latter. Although the importance of these galvanic currents with respect to pipe-line corrosion is not yet known, they are mentioned here as rather striking evidence of the electrochemical nature of the soil corrosion problem. The particular phase of the problem—namely, of determining the corrosiveness of a soil—involves a study of the factors in the soil which govern the electrochemical process of soil corrosion. By ascertaining the effect of these factors it is hoped that better ideas may be acquired toward the development of proper methods of reducing this corrosion loss.

Review of Principles Underlying Corrosion of Iron

The essential electrochemical reaction which occurs in the corrosion of iron, as proposed by Whitney (*9*), is represented by the following equations:

$$Fe + 2H^+ = Fe^{++} + 2H \qquad (1)$$

or

$$Fe + 2H_2O = Fe(OH)_2 + H_2 \qquad (2)$$

More recently Sweeney (*7*) has shown by thermodynamic reasoning that there is an electromotive force of 0.168 volt tending to drive iron into solution in accordance with Equation 2. Iron would therefore be expected to dissolve in water with the formation of ferrous hydroxide and liberation of hydrogen as a gas.

Shipley (*6*) and others have shown that corrosion of iron does occur in the absence of oxygen and that hydrogen gas is liberated during the process. More recently the writer (*2*) has shown that the volume of hydrogen gas liberated by the action of soil on iron is definitely related to the character of the soil.

The well-known fact, pointed out by Walker (*8*), that the liberated hydrogen may be removed as such or may be oxidized by air, explains how Reactions 1 and 2 may be continued.

From this brief review of existing theory it would appear that the rate of soil corrosion is probably related to the rate at which the hydrogen is produced and removed from the surface of the metal.

Soil Conditions Governing Corrosion

If our theory is true, then any factors which control the rate at which hydrogen is produced and removed are likely to determine the rate of corrosion. The one essential material for corrosion is water. It supplies the hydrogen. Under conditions otherwise the same, the principal factor which determines the rate at which hydrogen is produced is the hydrogen-ion concentration at the surface of the metal. The duration of this hydrogen production depends upon the total amount of acid available and also on the possibility of using the acid repeatedly through the process of hydrolysis. The rate of removal of the hydrogen from the zone of action depends upon its rate of diffusion away as hydrogen or upon its rate of oxidation.

The materials in the soil which are likely to exert a controlling effect on these processes may be listed as follows:

(1) Acidity, which involves both the hydrogen-ion concentration and the total quantity of material capable of supplying hydrogen ions.
(2) Air.
(3) Salts, which may either hasten or retard corrosion, depending upon their nature and concentration.
(4) Organic material.
(5) Soil-moisture conditions, which include rainfall, surface and subsurface drainage, retentive power of the soil for moisture, etc.
(6) Particle size or texture.

Obviously, the effect of all these factors cannot be studied by varying each of them separately and ascertaining the effects of such variations in one given case. Neither is it easy to compare different cases of corrosion and ascertain the individual effects of each factor. It appears hopeless to obtain even the simplest correlation of corrosion effects with any one of these factors without involving the others. In further consideration, let us see which of these factors may be evaluated with sufficient accuracy to differentiate soils from each other. We find that acidity, salt content, and particle size appear to be the only important factors which might be susceptible to quantitative determination and mathematical treatment.

On the basis of particle size or soil texture, soils have been classified into sands, silt loams, clays, etc. Comparison of corrosion losses with soils of different texture have shown that there is no apparent relation of corrosion to texture except as it affects other properties. This leaves soil acidity and salt content for consideration.

For reasons previously given, soil acidity should indicate corrosiveness, while salt content may or may not be an index to corrosiveness, depending upon the nature of the salt. In order to study the effect of either one of these factors it would be desirable to select those soils in which the other factor is negligible. The difficulty in this method is that we have no criterion by which to decide when a factor is negligible. Therefore, the most practical method of study would appear to lie in an effort to establish a trend in acidity or salt content with increasing corrosiveness.

The result of such an attempt is shown in Figure 1, in which the Bureau of Standards data (*3*) are used. A list of the soils with their numbers and locations are given in Table I. The soil numbers in all three graphs are arranged in the order of the "average weighted rate of corrosion of wrought steel and iron specimens."

Note—This "average weighted rate" was computed by finding the sum of all the losses in weight per unit of area suffered by the wrought specimens during the 2-, 4-, and 6-year periods; this sum was then divided by the sum of all the three periods of burial. The quotient thus obtained gives an average in which the individual losses are weighted in proportion to the period of burial.

The perplexity involved in attempting to establish any trend in either acidity or salt content with corrosiveness is made apparent by comparing these graphs.

Table I—Soils and Their Locations

No.	Soil	Location
1	Allis silt loam	Cleveland, Ohio
2	Bell clay	Dallas, Texas
3	Cecil clay loam	Atlanta, Ga.
4	Chester loam	Jenkintown, Pa.
5	Dublin clay adobe	Oakland, Calif.
6	Everett gravelly sandy loam	Seattle, Wash.
7	Fairmount silt loam	Cincinnati, Ohio
8	Fargo clay loam	Fargo, N. D.
9	Genesee silt loam	Sidney, Ohio
10	Gloucester sandy loam	Middleboro, Mass.
11	Hagerstown loam	Baltimore, Md.
12	Hanford fine sandy loam	Los Angeles, Calif.
13	Hanford very fine sandy loam	Bakersfield, Calif.
14	Hempstead silt loam	St. Paul, Minn.
15	Houston black clay	San Antonio, Texas
16	Kalmia fine sandy loam	Mobile, Ala.
17	Keyport loam	Alexandria, Va.
18	Knox silt loam	Omaha, Nebr.
19	Lindley silt loam	Des Moines, Iowa
20	Mahoning silt loam	Cleveland, Ohio
21	Marshall silt loam	Kansas City, Mo.
22	Memphis silt loam	Memphis, Tenn.
23	Merced silt loam	Buttonwillow, Calif.
24	Merrimac gravelly sandy loam	Norwood, Mass.
25	Miami clay loam	Milwaukee, Wis.
26	Miami silt loam	Springfield, Ohio
27	Miller clay	Bunkie, La.
28	Montezuma clay adobe	San Diego, Calif.
29	Muck	New Orleans, La.
30	Muscatine silt loam	Davenport, Iowa
31	Norfolk sand	Jacksonville, Fla.
32	Ontario loam	Rochester, N. Y.
33	Peat	Milwaukee, Wis.
34	Penn silt loam	Norristown, Pa.
35	Ramona loam	Los Angeles, Calif.
36	Ruston sandy loam	Meridian, Miss.
37	St. Johns fine sand	Jacksonville, Fla.
38	Sassafras gravelly sandy loam	Camden, N. J.
39	Sassafras silt loam	Wilmington, Del.
40	Sharkey clay	New Orleans, La.
41	Summit silt loam	Kansas City, Mo.
42	Susquehanna clay	Meridian, Miss.
43	Tidal marsh	Elizabeth, N. J.
44	Wabash silt loam	Omaha, Nebr.
45	Unidentified alkali soil	Casper, Wyo.
46	Unidentified sandy loam	Denver, Colo.
47	Unidentified silt loam	Salt Lake City, Utah

It is desirable to point out at this time that the general problem here is somewhat different from the usual problem in soil corrosion. Here we are attempting to compare data which have been obtained in widely distributed areas over the whole United States where climatic conditions are very different. In ordinary practice the climatic conditions over a small area would not vary over such a wide range, so that the method of comparison of data used in the previous graphs might lead to more definite conclusions. For our purpose, however, a different point of view must be taken.

Relation of Rainfall to Causes of Corrosion

In studying a group of variables, such as the corrosiveness, acidity, and salt content, etc., the problem is simplified if we can select one independent variable upon which the others largely depend. Between widely distributed areas rainfall may be considered as such an independent variable. Certainly most of the factors in the soil which govern corrosion are determined to a very large extent by rainfall. Heavy rainfall tends to extract the salts from the soil and carry them away; it tends toward acidity; it encourages accumulation of organic matter. In dry regions salts accumulate, acidity decreases, and organic matter becomes scarce.

An attempt to correlate the corrosiveness, acidity, and salt content with rainfall is shown in Figure 2. The soil numbers (see Table I) are arranged in the order of the increasing average annual rainfall of the regions in which the soils are located. The rainfall given here represents the average of all annual records obtained by the Weather Bureau for each location. The percentage of soluble salts in graph (7) was determined by the Bureau of Soils by an electrical conductivity method. The pH values in graph (5) were also determined by the Bureau of Soils using an electrometric method. (The averages of the pH values and salt content given in Table 2 of Bureau of Standards *Tech. Paper* 368 were used here.)

The values given here for both the pH value and soluble-salt content may or may not be representative of the locations from which the soil samples were taken. These quantities sometimes vary over a wide range within small depths. Thus, in the case of soil 5, we have the following wide variations:

Table II—Variation in pH and Salt Content of a Soil

Depth	pH	Soluble Salts	Depth	pH	Soluble Salts
Inches		*Per cent*	*Inches*		*Per cent*
0–10	6.0	0.039	24–36	6.9	0.052
0–12	5.3	0.021	36–48	7.7	0.150
10–30	5.9	0.044	48–60	8.4	0.180
12–24	5.2	0.030	60–72	8.2	0.174

In graph (6) two sets of pH values, determined by the writer using a colorimetric method, are given. For this purpose standard buffer solutions and indicators were used.

In graph (7) it may be seen that the salt content tends to decrease with heavy rainfall. The four notable exceptions to this rule—soils 33, 43, 27, and 29—are all poorly drained soils in which salts have accumulated even though the rainfall is heavy.

In graphs (5) and (6) of Figure 2 it is clear that the pH values decrease from the neighborhood of 7 and above, in arid regions, to about 5 in humid regions. Particular attention is called to the pH values determined in a 5 per cent potassium chloride solution, which are lower in practically all soils than those obtained in distilled water. The differences between these pH values are generally greater where the pH value is low. The reason for using potassium chloride is discussed later in this paper.

From graph (4), which represents the relative corrosiveness of the soils, it will be observed that any attempt to correlate corrosiveness of these soils with the total salt content fails. When the corrosiveness and salt content are both high, the corrosiveness may be attributed to a high salt content, but the converse is not true, as is evident in the cases of soils 45, 46, 35, 47, 5, and 8. That is, a high salt content does not always indicate a high degree of corrosiveness.

Inasmuch as the salt content in these soils was determined by an electrical conductivity method, and in view of the evidence that a high salt content does not necessarily signify corrosiveness, it would appear that any conductivity method used for determining corrosiveness is likely to be misleading unless the nature of the salt is known. Such a method should, therefore, be accompanied by a chemical analysis of the salts present. Further work on the relation of corrosiveness of these soils to salt content has therefore been postponed until further information about the nature of the salts has been obtained. The present discussion is therefore limited almost entirely to soils of humid regions.

Wherever there is a peak in graph (4) in humid regions there is a corresponding lower pH value in graph (6). Thus, above a certain rainfall of about 30 inches, we note the following soils where acidity seems to be related to corrosion: 1, 4, 17, 43, 42, 37, 29, and 16. The higher pH values also generally correspond to a lower corrosion loss in the humid soils. Several soils, however, particularly 7, 19, and 40, are exceptions and will be discussed later. In the case of soils 43 and 29 the salt content may also be an important factor.

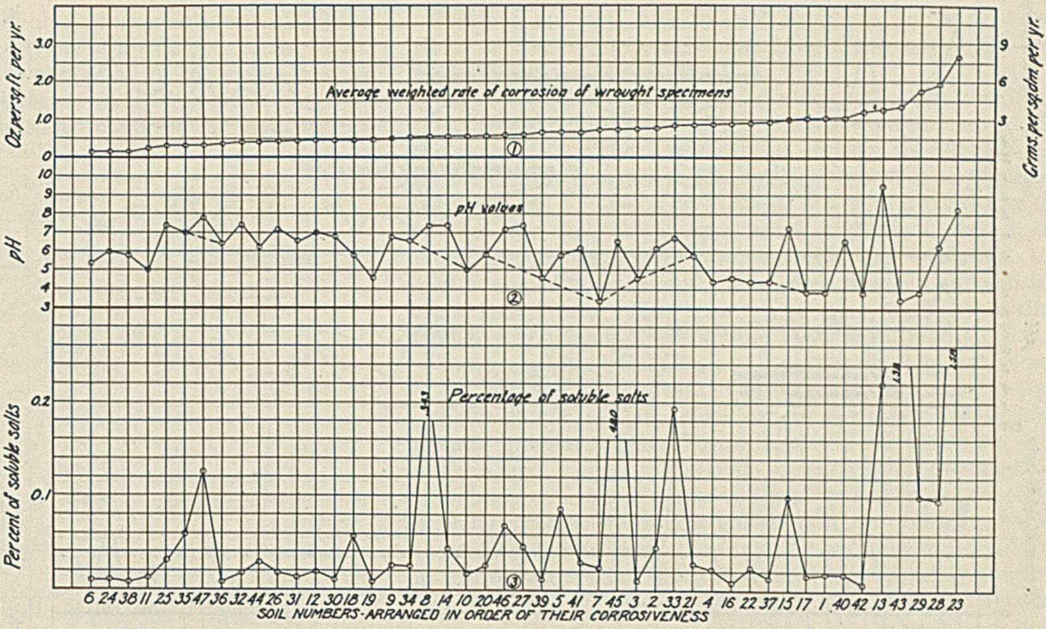

Figure 1—Comparison of Rates of Corrosion with Acidity and Salt Content of Soils

As judged by the relations shown by the preceding graphs, it seems apparent that rainfall is an important factor in determining the acidity and, since there is fair correlation between corrosiveness and acidity, a study of methods for determining acidity from a corrosion standpoint seemed justified.

Methods of Estimated Soil Acidity

As Shipley (*6*) pointed out, the pH value should be a determining factor in controlling the rate of corrosion while the total acidity should determine the duration of the corrosive action. For this reason a low pH value would not necessarily mean that a soil is corrosive for any appreciable period of time. In order for a low pH value to be an effective factor in maintaining corrosion, there must be sufficient organic or inorganic colloidal matter or other material present to maintain or "buffer" the pH at its low value. Since the acidity of a soil resides chiefly in its colloidal portion, an approximate idea of the total acidity may be acquired by taking both the pH value and the content of colloidal matter into account.

The colloidal content of a soil requires a laborious method for its accurate determination, but a simple method has been suggested by Bouyoucos (*1*) which gives results of interest in connection with the present problem. It consists in stirring for several minutes a sample of the soil in a dilute solution of potassium hydroxide with a motor-driven propeller, and then pouring the soil suspension into a tall cylinder and inserting a hydrometer. After a definite period of time the apparent density of the suspension is read off the hydrometer which is calibrated to give the content of soil colloid directly. While this method is empirical, it gives comparative results (Table III).

It will be noted that those soils which are corrosive because of acidity are high in colloidal material, with the exception of the two sandy soils, 37 and 16. These two soils are wet and contain considerable organic material. With these exceptions it would appear that when the pH value is low and the colloidal content is high corrosiveness may be expected.

Although a rough approximation of the total acidity of a soil may be made on the basis of its pH value and colloidal content, it seems very desirable to consider the possibility of determining the total acidity directly by titration. Several conditions make a titration with an indicator difficult, the chief one being that it is practically impossible to detect the color change in the turbid liquid at the end of the titration.

Table III—Percentage of Colloidal Matter[a] in Soils according to Method of Bouyoucos

SOIL	PER CENT	SOIL	PER CENT	SOIL	PER CENT	SOIL	PER CENT
1	64	13	18	25	31	37	7
2	47	14	3	26	50	38	6
3	43	15	63	27	91	39	16
4	25	16	21	28	29	40	50
5	45	17	76	29	24	41	44
6	11	18	29	30	42	42	45
7	70	19	39	31	1	43	51
8	66	20	44	32	23	44	32
9	36	21	43	33	20	45	..
10	16	22	33	34	42	46	7
11	52	23	18	35	20	47	54
12	9	24	7	36	38		

[a] Determined by S. P. Ewing, assistant physicist, Bureau of Standards.

Considerable attention was given to experimenting with a hydrogen electrode for obtaining the end point in titration. A motor-driven propeller was used to insure thorough mixing of the soil and standard solution of alkali. Steady readings were not obtained unless a salt was used. The use of potassium chloride permitted consistent readings to be obtained and to be repeated with a fair degree of precision. When the salt was added, the soil settled more quickly after stirring so that an indicator might be used with fair results, especially with the more sandy soils.

It has been known for many years that some soils react with neutral salts, such as potassium chloride, to produce acid. The usual explanation for this behavior is that the basic ions of the salt are exchanged for the hydrogen ions of the soil and the process is designated by soil chemists as "base exchange." Through base exchange, therefore, hydrochloric acid may result from the action of soils on potassium chloride. The process of base exchange is considered by many physical chemists to be one of adsorption. It seems reasonable to suppose that this affinity of a soil for basic ions might also include ferrous ions. We have, however, no evidence on this point. From graph (6) we see at once the marked effect of a 5 per cent solution of potassium chloride in decreasing the pH value of a soil in many cases.

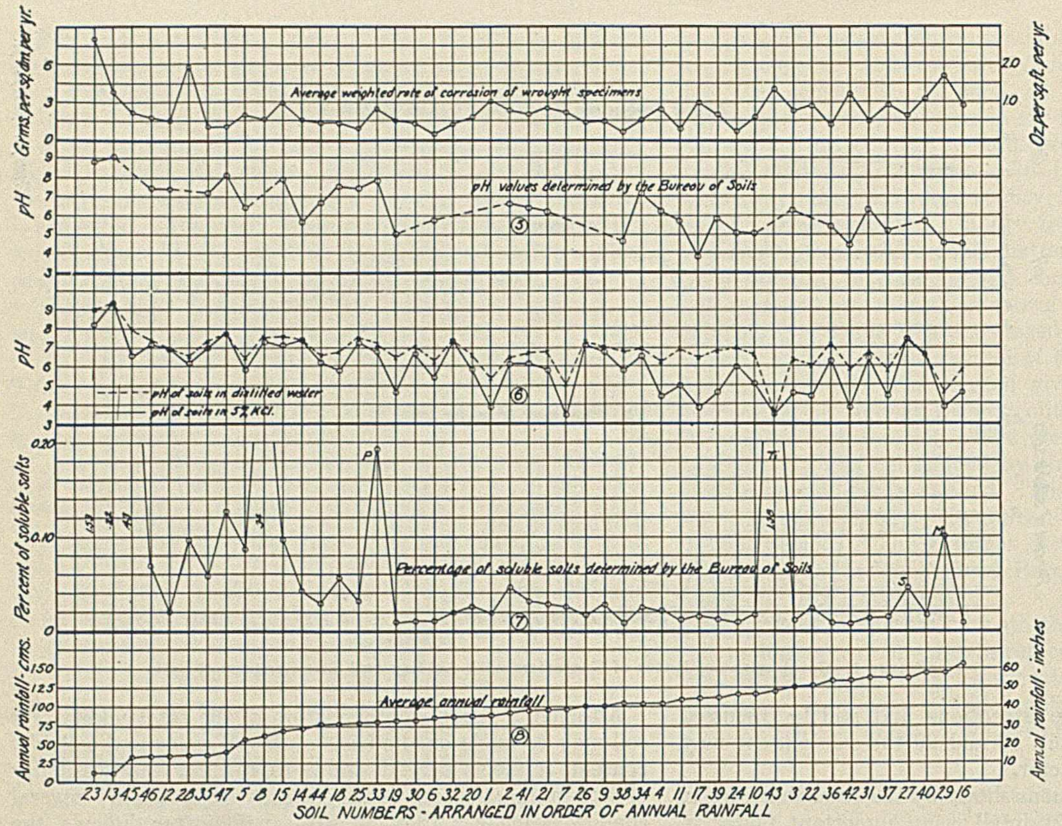

Figure 2—Comparison of Rates of Corrosion with Acidity and Salt Content of Soils as Related to Annual Rainfall

Since the process of base exchange involves a transfer of the hydrogen ions from the soil particles to the aqueous solution, the hydrogen-ion concentration of the solution is therefore increased by the addition of potassium chloride. Since such an increase in hydrogen-ion concentration is related to the number of hydrogen ions attached to the soil particles, the difference in pH value of the soil in water and in a potassium chloride solution should serve as an approximate measure of the total acidity of the soil.

In titrating the total acidity of a soil in the presence of potassium chloride, the consumption of the alkali is, therefore, due to the hydrochloric acid formed by base exchange. In Figure 3 we have a number of titration curves obtained with Susquehanna clay which are of a shape characteristic of a strong acid. For making these titrations, a hydrogen electrode consisting of a platinized wire and supplied with hydrogen from a tank of the compressed gas was used. This electrode, dipping in the soil suspension in a 5 per cent solution of potassium chloride, was measured against a 0.1 *N* calomel electrode. The electric potential of the hydrogen-calomel cell was balanced against a dry cell by the use of a slide-wire rheostat. The desired potential was then read off a millivoltmeter connected across the rheostat. This method is thus based on the potentiometer principle, but is direct-reading and sufficiently precise for this work. The soil was vigorously stirred with a motor-driven propeller after each addition of alkali, but stirring was stopped while the reading was being taken. The time necessary for completion of the reaction between the soil and alkali requires further study, but it is believed that the reaction was practically complete and the results here obtained during the time necessary for a titration are comparable.

All readings made during the titration indicated in Figure 3 were plotted in order that some idea may be obtained as to their consistency. The readings at the beginning of each titration were somewhat erratic, but as neutrality was approached they became more steady. The amount of alkali required for neutralization is very nearly proportional to the weight of soil taken. Using 20-gram samples, additional titrations were made on all of the forty-seven soils used in the Bureau of Standards investigation. Titration curves for a few typical soils are shown in Figure 4.

A number of soils show the presence, in different amounts, of strong acid, similar to that observed in Susquehanna clay. Some of them are 1, 3, 7, 16, 17, 19, 22, 42, 43, and *X*. With the exception of 7 and 19, these soils show high rates of corrosion. The salt content is very low except in the case of 43 and *X*. The latter is a soil which is reported to be very corrosive. Soil 43 exhibited no decrease in pH value when treated with potassium chloride.

Several soils, typified by 33 and 37 in Figure 4, combine with considerable alkali without appearing to reach any end point. Soil 29 also takes up considerable alkali, but it reaches a fairly definite end point. All three of these soils contain much organic material and exert a strong buffer effect at a pH of about 8.

Many of the soils gave titration curves similar to those for 38, 14, and 32, which do not have the shape characteristic of a strong acid or of any buffer material. They resemble the

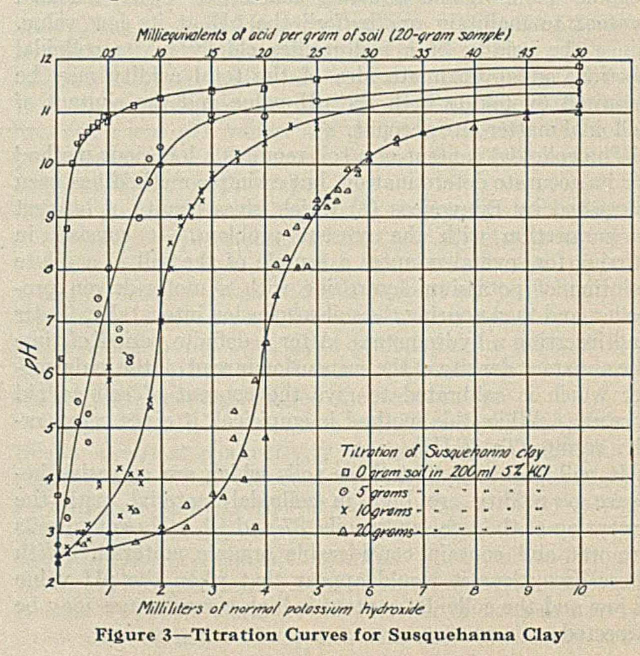

Figure 3—Titration Curves for Susquehanna Clay

curve obtained by adding alkali to a solution of potassium chloride alone, but the steepness of their slopes seems to bear some relation to the colloidal content of the soils. Because of this tendency, there is reason to believe that some alkali is taken up by the soil in some manner other than by neutralization.

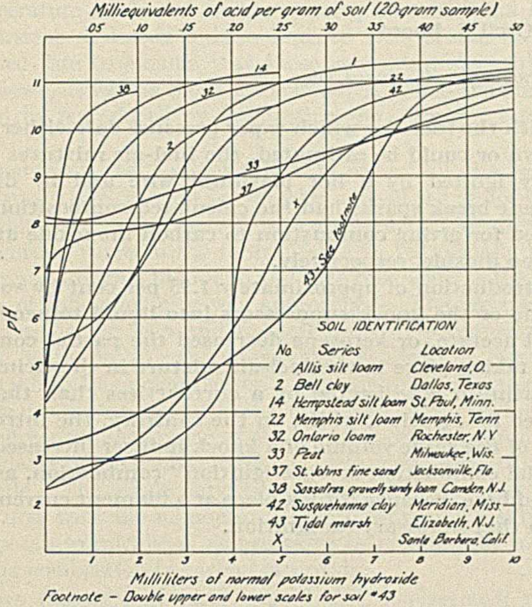

Figure 4—Titration Curves for Different Soils

It is therefore necessary that these titration curves be interpreted with the understanding that other reactions besides acid-alkali neutralization may occur. This will be apparent if we ask the question—what pH value should be taken as the end point in these titrations? In considering an answer to this question let us ask a related question—what is the maximum pH value at which iron corrodes?

Shipley (*5*) has demonstrated experimentally that in the absence of oxygen iron will corrode until a pH value of 9.4 is reached, this value corresponding to the solubility product of ferrous hydroxide. The writer has also observed that wet mixtures of soil and pulverized iron continue to evolve hydrogen until a pH value of 9.4 or greater is reached. It would therefore seem logical to consider a pH value of 9.4 as the end point in the above titrations. Accordingly, the total acidity of soil 42 would be about 0.27 milli-equivalents of acid per gram of soil.

Relation of Total Acidity to Hydrogen Evolution

The property, possessed by many soils, of reacting on iron with evolution of hydrogen gas has been shown by the writer (*2*) to be a very definite property of the soil. This reaction has been found to continue until the alkalinity of the adjacent solution rises to a pH value of about 9.4 or 9.6. If the amount of hydrogen evolved is determined by the total acidity of the soil, we should be able to demonstrate such a relation by plotting the volume of hydrogen evolved against the total acidity. This has been done in Figure 5. Here the volume of hydrogen evolved in 20 days from a mixture of 7.5 grams each of soil and iron is plotted against the volume of normal alkali solution required to raise the pH value to 9.4 in the case of each soil. These points are indicated by the soil numbers which appear on the figure. There seems to be no question regarding the general relation between the ability of a soil to liberate hydrogen from iron and to take up alkali. The outstanding exceptions are few, and in each case are corrosive soils which are very high in organic matter. The reason for these exceptions is not known.

While the relation shown in Figure 5 is indicative, the data presented should be considered tentative since neither of the reactions involved was carried entirely to completion. Before definite conclusions can be safely drawn as to whether the measured volume of gas liberated is a measure of the total acidity of a soil, these experiments ought to be repeated under conditions which would permit gas evolution to continue until it ceases and the reaction of alkali and soil to reach equilibrium. It is believed, however, that the results would not be much different from those already obtained.

The reason that soils 7 and 19 do not show higher rates of corrosion is not known. The soil moisture may be the decisive factor in such cases where corrosion agents are already present. Water being essential to corrosion, its absence may reduce the activity of such agents to a part-time basis. Access of water to the corroding metal depends upon local conditions, such as surface and subsurface drainage, the power of the soil to absorb and retain moisture, capillary migration, etc.—all of which should be more definitely known. In the case of another soil (40) the acidity does not appear high, but the rate of corrosion is considerable. The salt content is found to be low also, but the soil is always very wet. Here again the soil-moisture conditions may be the decisive factor. The soil-moisture problem is closely allied with the conditions which permit the access of air.

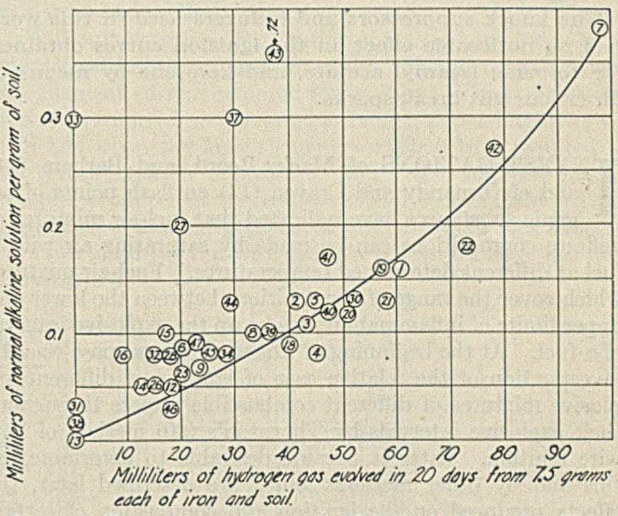

Figure 5—Comparison of Property of Soils of Liberating Hydrogen, When Reacting with Iron, with Their Property of Combining with Potassium Hydroxide

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Synthetic Methanol Plant Proposed in Belgium

Assistant Trade Commissioner George W. Berkalew, Brussels, has advised the Department of Commerce that production of synthetic methanol is contemplated by the firm Evence Coppée at its coke-oven plant at Willebroeck. This installation, when completed, will be the first in Belgium for the synthetic production of methanol.

Effects of Knock-Suppressing and Knock-Inducing Substances on the Ignition and Partial Combustion of Certain Fuels[1,2]

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Hot-wire ignition curves were determined for toluene, isoamyl acetate, and kerosene between the lower and upper limits of inflammability. The fuel-air mixtures investigated were produced by a vapor pressure method which is described and shown to be applicable to the continuous and reproducible preparation of such a series of mixtures.

The current required by an electrically heated platinum wire for ignition of the most easily ignitible mixture of air and toluene, isoamyl acetate, or kerosene was increased by the addition to the fuel of a knock suppressor such as lead tetraethyl or selenium diethyl. On the contrary, the addition of one of the knock inducers decreased the hot-wire ignition current.

The knock suppressors and inducers used in this work had no noticeable effect on the ignition curves obtained for toluene, isoamyl acetate, and kerosene by means of direct-current break sparks.

With the fuels for which vapor pressure data either were known or could be estimated, the fuel-air mixtures most easily ignited by a hot platinum wire and by direct-current break sparks had the calculated compositions required for giving combustion to carbon monoxide and to carbon dioxide, respectively.

Introduction of approximately 1.95 per cent by volume of one of the knock suppressors into liquid toluene, isoamyl acetate, or kerosene decreased the partial combustion taking place in the fuel-air mixture in the vicinity of a platinum wire heated by a current less than that required for ignition, while, on the contrary, the introduction of the same volume of a knock inducer increased this partial combustion or "pre-ignition" combustion, as it is called here, because it took place at a filament current less than that necessary for ignition.

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INVESTIGATIONS of Mack, Boord, and Barham (*11*) and of Ormandy and Craven (*14*) on flash points of organic substances have indicated that fuel-air mixtures of definite compositions can be made by saturating air with a fuel at different determined temperatures. Fuel-air mixtures which cover the range of compositions between the lower and upper limits of inflammability make up the explosive interval of a fuel. At the beginning of this work, its purpose was the investigation of the relative ease of ignition of different explosive mixtures of different combustible vapors throughout their explosive intervals by Thornton's (*20*) method of hot-wire ignition. Later it became desirable to determine, by this and by other methods which are described later, the effects produced on the ignition and combustion of certain combustible vapors by the addition of different knock suppressors and knock inducers.

Hot-Wire Ignition

Apparatus—The apparatus used is shown in Figure 1. Compressed air purified by passage through the soda-lime tube, *A*, and dried by calcium chloride tube, *B*, was regulated by a constant-pressure device, *C*, and flowmeter, *D*, so that it entered through the saturator, *E*, similar in principle to that devised by Stromeyer (*16*), containing 50 cc. of fuel, and bubbled up through 15 cc. of the same fuel in the bottom of the ignition tube, *F*, at a constant, uniform rate of 115 cc. per minute. The ignition tube and saturator were suspended in a bath of water, or later of glycerol for work with fuels having high flash points, so that the temperature of the fuel could be raised by successive increments in order to produce a series of mixtures having progressively increasing fuel concentrations throughout the explosive interval. The temperature of the fuel was measured by a mercury thermometer adjusted so that the bulb was immersed completely in the fuel in the ignition tube. The ignition unit, *G*, consisted of a 20 mm. length of No. 31 B. & S. gage (0.227 mm. diameter) platinum wire clamped by and suspended between the lower split ends of two parallel, vertical brass rods. Palladium wire of the same size was used also in a few experiments. The upper ends of the brass rods were connected by insulated copper wires to the terminals of a 10-volt storage battery with suitable resistances, R_1 and R_2, divided in parallel and with the ammeter in the shunt circuit. The ammeter could be read to 0.05 ampere over a range of 5 amperes. In some of the later work current was obtained from a 120-volt d. c. generator and the ammeter and all of the resistance were then connected in series.

Procedure—In order to carry out a determination, the bath surrounding the saturator was heated until the fuel in the saturator and ignition tube was at a constant temperature 2 or 3 degrees above that required to produce the leanest explosive mixture. Then the ignition circuit was closed and the resistance was decreased until sufficient current flowed through the platinum wire to heat it to the temperature necessary to cause ignition. After several readings of the ignition amperage were taken at this temperature and recorded, the saturator temperature was increased 5° C., and the observation was repeated. At any saturator temperature and for a given wire, successive readings usually did not vary by more than 0.1 or 0.2 ampere. The entire explosive interval was explored by raising the temperature of the fuel by increments of 5° C. and measuring the current required for ignition. A duplicate determination over the entire explosive interval was made under the same conditions as a check.

After the ignition amperages of a fuel had been determined over the explosive interval and duplicated, 1 cc. of a knock suppressor or knock inducer was added to the fuel in the ignition tube, and the ignition amperages were redetermined over the same explosive interval using the same ignition filament. Although this method of introducing knock suppres-

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[1] Presented under the title "Effect of Knock-Suppressing and Knock-Inducing Substances on the Combustion of Certain Pure Fuels" before the Division of Petroleum Chemistry at the 74th Meeting of the American Chemical Society, Detroit, Mich., September 5 to 10, 1927. Received March 23, 1929.

[2] Abstracted from the dissertation presented by Mr. Schaad to the Graduate School of The Ohio State University, June, 1926, in partial fulfilment of the requirements for the Ph.D. degree.

[3] Present address, Universal Oil Products Co., Chicago, Ill.

sors and knock inducers was very convenient, it is apparent that the concentration of the added substance would probably be higher in the rich than in the lean fuel-air mixtures. It is conceivable, however, that the ratio of the concentration of the added substance to that of the fuel in the different mixtures might remain fairly constant throughout the explosive interval. This condition would be approached if the temperature coefficient of the vapor pressure of the knock suppressor or knock inducer equaled that of the fuel. It seemed safe to assume that these concentrations, although unknown, as well as those of the undoped fuel in the mixtures could be reproduced by duplicating the saturator temperatures.

Results with Undoped Fuels—When all the ignition amperages were plotted as ordinates against the temperatures at which air was saturated with a given fuel as abscissas, an ignition curve in the form of an area fell, usually rather sharply, through a minimum and then rose again as the upper limit of inflammability was approached. The ignition amperages for the lean and rich mixtures were approximately equal, while that for the minimum of the ignition curve was from 0.5 to 1.5 amperes lower. The minimum of the ignition curve usually was not at that temperature which on the basis of the vapor pressure curve of the fuel should have produced the ideal explosive mixture for complete combustion to carbon dioxide. The whole curve was displaced toward the richer mixtures with the minimum falling usually at the saturator temperature calculated as necessary to produce the mixture giving combustion to carbon monoxide.

Two factors may have caused this displacement of the minimum of the ignition curve. First, the air stream may not have been saturated completely with the vapor of the fuel, although all attempts to secure more complete saturation did not change the displacement. Second, a partial combustion or "burn-out" may have taken place in the vicinity of the heated wire, at temperatures below that required for ignition, during the time interval necessary for adjusting the resistance to give the current necessary for ignition. If, for example, the most easily ignited mixture was that with a composition calculated for giving combustion to carbon dioxide, any preliminary burn-out of this mixture in the zone surrounding the heated filament would have made the remaining mixture more difficult to ignite. In order to offset the burn-out, the initial fuel concentration corresponding to the most easily ignitible fuel-air mixture, and consequently the saturator temperature needed to produce it, would have been higher than if no burn-out of fuel took place.

Hot-wire ignition curves were obtained for *n*-propyl, *n*-butyl, and isoamyl alcohols, toluene (Figures 2 and 3), isoamyl acetate (Figure 4), kerosene (Figures 5 and 6), diethyl maleate, and diethyl fumarate. All the curves shown in Figures 2 to 6, inclusive, were obtained by using platinum ignition filaments. The general form of the ignition curves was the same in every case. Naturally, the saturator temperatures required to produce explosive mixtures of the different fuels with air were different because they were determined by the vapor pressures of the different fuels. No difficulty was experienced in reproducing the ignition curves of any of the fuels as long as the same filament was used. Different filaments even from the same sample of wire gave slight differences in ignition amperage. Therefore, it was always necessary to reproduce the fuel ignition curve with each new filament before adding the knock inducer or knock suppressor and determining the effect produced by such an addition.

Results with Doped Fuels—In the presence of the organo-metallic knock suppressors the heated ignition filament deteriorated more rapidly than when the knock inducers were employed with the different fuels. A few filaments lasted long enough to permit ignition curves to be determined for an undoped fuel and for the fuel containing a knock inducer and a knock suppressor, respectively. In most cases an ignition curve of a given fuel could be determined and duplicated, and then the ignition curve of the fuel doped with either a knock inducer or suppressor could also be obtained and checked before the filament would become weakened and burn out. Most of the burning out of filaments was due to excessive current used in attempting to ignite the very rich mixtures.

The knock suppressors lead tetraethyl (Figure 2), lead tetramethyl, selenium diethyl (Figure 4), and aniline (Figure 5), and the knock inducer isoamyl nitrite (Figures 3 and 4) were used with toluene, isoamyl acetate, and kerosene. Another knock suppressor, ethyl iodide, and a knock inducer, propyl nitrite, were used with toluene. The knock inducer nitrobenzene (Figure 6) was used with isoamyl acetate, kerosene, and diethyl fumarate, while *o*-nitrophenol produced the effect of a knock inducer with diethyl fumarate. Phenyl iodide gave the effect of a knock suppressor with both diethyl fumarate and diethyl maleate.

Without exception, the addition of 1 cc. of any of the above-mentioned knock suppressors to the different fuels increased the filament current required for ignition. The ignition current was from 0.5 to 2.0 amperes higher, depending upon the fuel and upon the knock suppressor, than that required by the given ignition filament to ignite the undoped fuel-air mixture produced at the same saturator temperature. These results show that the presence of any of these knock suppressors increased the hot-wire ignition temperatures of the fuels investigated.

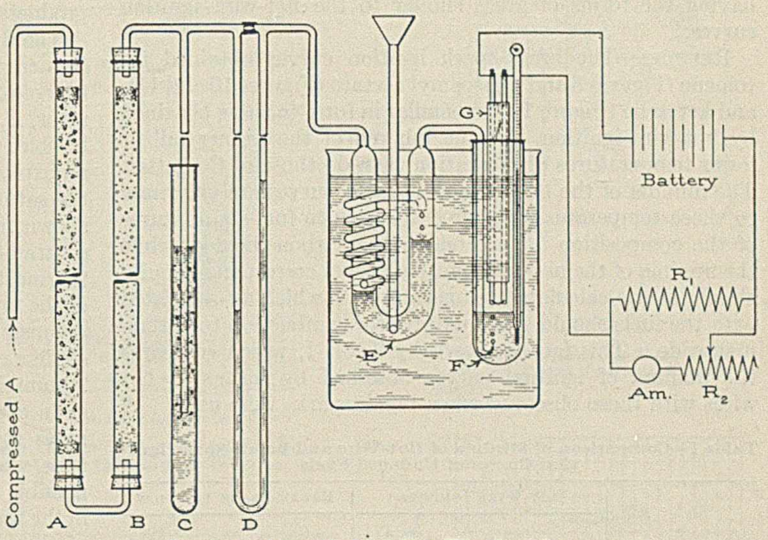

Figure 1—Apparatus for Hot-Wire Ignition

On the contrary, the introduction of the knock inducers into the different liquid fuels lowered the amperage required for ignition by a hot wire. The smallest lowering (0.15 ampere) of the ignition amperage was produced by nitrobenzene in isoamyl acetate and the greatest (1.0 ampere) by propyl nitrite in toluene. Thus the addition of the knock inducers lowered the hot-wire ignition temperatures of the different explosive fuel-air mixtures.

In a preliminary report several years ago, the authors (*2*) expressed the same conclusion that the addition of certain knock suppressors increases the hot-wire ignition temperatures of toluene, isoamyl acetate, and *n*-propyl alcohol, whereas the presence of a knock inducer such as propyl nitrite, isoamyl nitrite, or nitrobenzene decreases these temperatures.

Break-Spark Ignition

Apparatus and Procedure—In attempting to determine whether the displacement of the minima of the hot-wire ignition curves toward richer mixtures was due to a burn-out of the combustible vapor in the vicinity of the heated wire, this means of ignition was replaced by the direct-current break-spark gap shown in Figure 7. The remainder of the apparatus was kept the same as for hot-wire ignition and the procedure differed only in the following method of ignition. In making a determination with break-spark ignition, the rod *E* was turned by the small crank, *F*, until the brass springs at the lower ends of the brass rods were pressed together firmly. Then the switch was closed and the potential across the ignition circuit was adjusted to 110 volts by means of the two resistances connected in series. While a stream of 115 cc. of air per minute, saturated at a known temperature slightly above that necessary to produce the leanest explosive mixture, was passing up around the ignition unit in the ignition tube, the rod was turned quickly, so as to break the circuit and produce a spark at the gap between the brass springs. If ignition did not take place, resistance R_2 was decreased repeatedly so as to increase the ignition current by increments of 0.1 ampere until the minimum current required for ignition was reached. Several repetitions of this determination at a given saturator temperature were then made as a check. The ignition amperages were determined and duplicated at intervals of 5° C. throughout the explosive interval of a given fuel, and then 1 cc. of a knock suppressor or knock inducer was added and its effect determined in the same way as in the experiments on hot-wire ignition. All the results obtained in a given determination were plotted to give ignition curves having the forms of areas similar to the hot-wire ignition curves.

Results—The break-spark ignition curves obtained for toluene (Figures 8 and 9), isoamyl acetate (Figures 10 and 11), and kerosene (Figure 12) are similar in form to those obtained by hot-wire ignition, but the minima of the former fall at lower temperatures of saturation than do those of the latter. The minima of the break-spark ignition curves are very near to those temperatures required to produce fuel-air mixtures of the composition for combustion to carbon dioxide, while the minima of the hot-wire ignition curves corresponded quite closely to the calculated temperatures at which air saturated with the fuels should give mixtures for combustion to carbon monoxide. This fact is shown by Table I, which compares the minima of ignition curves obtained by means of hot wires with those observed when break sparks were used.

Table I—Comparison of Minima of Hot-Wire and Break-Spark Ignition Curves of Undoped Fuels

Fuel	Hot-Wire Ignition			Break-Spark Ignition		
	Number detd.	Minimum	Calcd. saturator temp. for combustion to CO	Number detd.	Minimum	Calcd. saturator temp. for combustion to CO_2
		° C.	° C.		° C.	° C.
Toluene	9	20–28	24.4	4	15	15
Isoamyl acetate	6	45–57	54	3	39–45	43
n-Propyl alcohol	2	41–45	38			32
n-Butyl alcohol	1	54	52			46
Isoamyl alcohol	1	55–62	58			52
Kerosene	6	75–90		4	65–80	

In connection with the minima of these ignition curves, attention should be called to Thornton's (*19*) results on the continuous-current break-spark ignition of mixtures with air of methane, ethane, propane, and butane, respectively. He stated that "each gas has the same minimum ignition current. The mixtures at which this occurs are in most cases near those for perfect combustion."

The addition to each of the above-mentioned fuels of either a knock suppressor, lead tetraethyl (Figures 8 and 12) or selenium diethyl (Figure 10), or a knock inducer, isoamyl nitrite (Figure 9), produced very little, if any, noticeable change in the ignition amperage and also little displacement of the minima of the ignition curves toward leaner or richer fuel-air mixtures except in the case of isoamyl acetate containing isoamyl nitrite (Figure 11).

The occurrence of the minima of the break-spark ignition curves at the saturator temperatures required for producing mixtures capable of giving combustion to carbon dioxide and the general lack of effect of both knock suppressors and knock inducers on these curves indicated that with hot-wire ignition probably a burn-out took place in the vicinity of the heated wire before the current required for ignition was reached, but that it was practically absent when ignition was effected by a momentary direct-current break spark. The marked effect which knock suppressors exerted on the hot-wire ignition curves seemed due to their influence in hindering the burn-out. Since the burn-out apparently took place at an amperage less than that required for ignition, it may be spoken of as preliminary or "pre-ignition" combustion. Knock suppressors seemed to hinder pre-ignition combustion while knock inducers apparently promoted it.

Pre-Ignition Combustion

Apparatus—Quantitative proof of pre-ignition combustion was obtained by passing a given fuel-air mixture over a platinum or palladium wire heated by an electric current less than that required for ignition, and determining the carbon dioxide, oxygen, and carbon monoxide in the partially burned gaseous products.

The apparatus (Figure 13) consisted of the same train as formerly used for purifying, drying, and saturating a regulated flow of compressed air with the vapor of a given fuel. The saturator, *E*, containing 50 cc. of fuel, was connected to a safety bubbler tube, *F*, partly filled by 15 cc. of fuel, so as to prevent an explosion in the ignition tube, *I*, from traveling back into the saturator. The ignition tube was replaced later by that shown in Figure 14 in order to keep the air stream always saturated with the fuel vapor at the temperature of the thermostat by preventing the cooling and partial condensation of the fuel-air mixtures. A d. c. generator supplied current at a constant potential of 110 volts, and at 20 volts in a few similar experiments, to the ignition filament consisting of a 20-mm. length of No. 31 B. & S. gage platinum wire, clamped, as in experiments on hot-wire ignition, between two parallel brass rods and extending across the center of the ignition tube, which had an opening at the bottom so as to prevent its possible destruction by an explosion within. This opening in the ignition tube was closed by a mercury seal while samples of the partially burned gaseous products were collected for analysis. A No. 31 gage palladium ignition filament was also used in a few experiments. Before sampling the combustion products, the water in the sampling bottles was saturated with them.

Procedure—In order to determine the pre-ignition combustion curve of a given fuel, the thermostat containing the saturator was set at the temperature corresponding to that of the minimum of the hot-wire ignition curve and kept constant to within 0.1° C. Then while a stream of 115 to 120 cc. of air per minute was passing through the saturator and ignition tube, the ignition circuit was closed and the resistances were adjusted so that enough current flowed through the

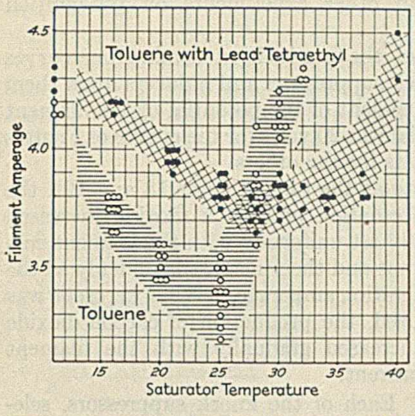

Figure 2—Effect of Lead Tetraethyl on Hot-Wire Ignition of Toluene

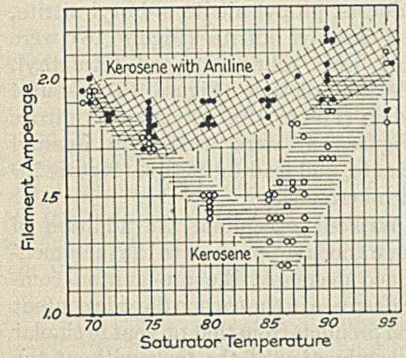

Figure 5—Effect of Aniline on Hot-Wire Ignition of Kerosene

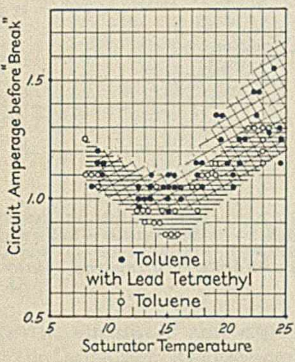

Figure 8—Effect of Lead Tetraethyl on Break-Spark Ignition of Toluene

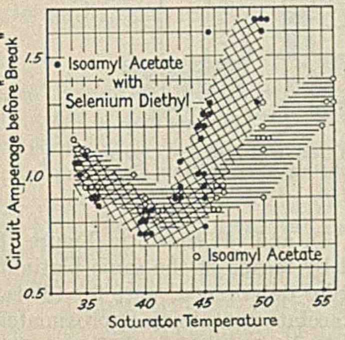

Figure 10—Effect of Selenium Diethyl on Break-Spark Ignition of Isoamyl Acetate

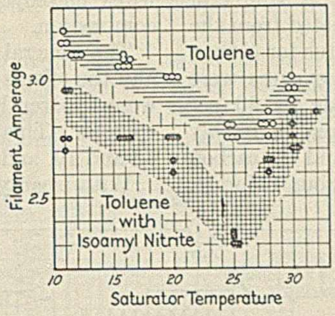

Figure 3—Effect of Isoamyl Nitrite on Hot-Wire Ignition of Toluene

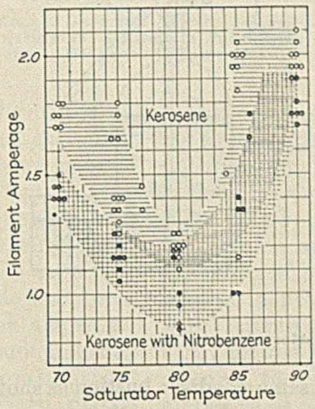

Figure 6—Effect of Nitrobenzene on Hot-Wire Ignition of Kerosene

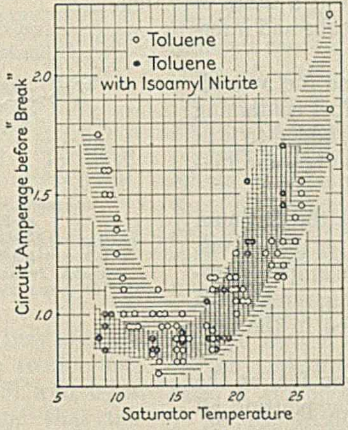

Figure 9—Effect of Isoamyl Nitrite on Break-Spark Ignition of Toluene

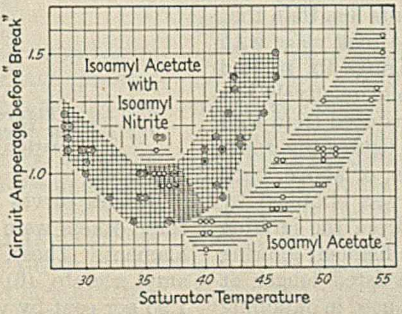

Figure 11—Effect of Isoamyl Nitrite on Break-Spark Ignition of Isoamyl Acetate

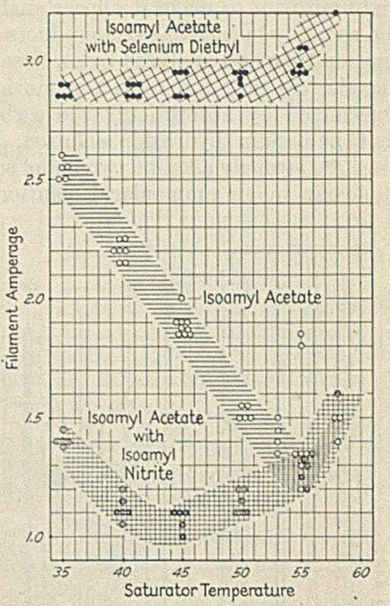

Figure 4—Effect of Selenium Diethyl and Isoamyl Nitrite on Hot-Wire Ignition of Isoamyl Acetate

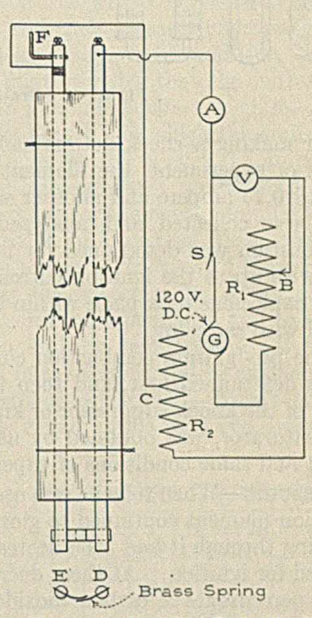

Figure 7—Ignition Unit Used in Break-Spark Ignition Experiments

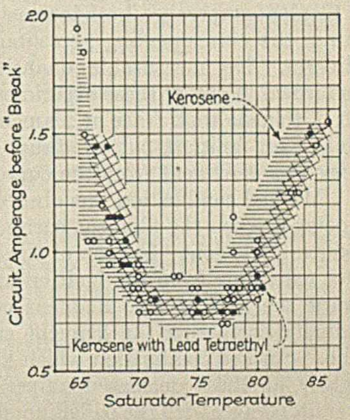

Figure 12—Effect of Lead Tetraethyl on Break-Spark Ignition of Kerosene

platinum wire to make it appear slightly red. A sample of the partially burned gaseous products was collected from the ignition tube and analyzed by an Orsat apparatus for carbon dioxide, oxygen, and carbon monoxide. These gases were determined by absorption: the carbon dioxide by 40 per cent potassium hydroxide solution, the oxygen in freshly prepared strongly alkaline pyrogallol solution, and the carbon monoxide in an ammoniacal solution of cuprous chloride. After making a check determination under the same conditions of experiment, the filament current was increased by 0.1 to 0.25 ampere and another sample of combustion products was collected and analyzed. Thus the pre-ignition combustion was determined for filament currents increasing stepwise up to the ignition current, but above it a series of mild explosions took place within the ignition tube and interfered with sampling.

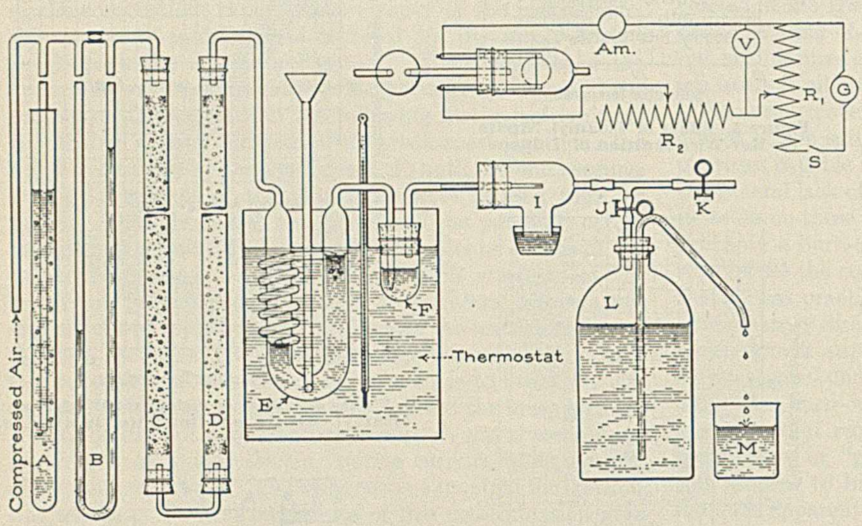

Figure 13—Pre-ignition Combustion Apparatus

The pre-ignition combustion curve of a given fuel was always determined first, and then that of the fuel containing 1 cc. of the knock suppressor or knock inducer, added to it in the saturator, was obtained by using the same ignition filament and same conditions of experiment.

Results—When toluene was used as the fuel, the platinum ignition filament continued to glow brightly after the current passing through it had been decreased from the amperage required for ignition. At these decreased amperages relatively high percentages of carbon dioxide were formed in the partially burned gaseous products.

The pre-ignition combustion curve of a given fuel at the chosen saturator temperature was obtained by plotting all the filament amperages, both increasing and decreasing values, against the corresponding percentages of carbon dioxide as ordinates. No measurable quantity of carbon monoxide was formed in any of these experiments. Very little combustion of toluene took place at filament currents less than that required for ignition, but an abrupt increase took place with ignition as is evident from the curves of Figures 15, 16, and 17. Marked combustion was observed also at relatively low amperages when the filament current was reduced from that producing ignition. In each of these three figures the upper curve extending from the ignition amperage, or above, back toward the axis of zero filament current was obtained by gradually decreasing the filament current from the ignition value. Surface combustion which kept the filament glowing brightly at these decreased amperages persisted longer at lower amperages with the palladium filament used in obtaining the curves shown in Figures 16 and 17 than with the platinum wires employed in all other experiments on pre-ignition combustion.

The general form of the pre-ignition combustion curves and the effects of knock suppressors and inducers upon them were apparently independent of the potential of the filament current. This potential was 20 volts for the curves of Figures 15 and 19, and 110 volts for the others.

With isoamyl acetate as the fuel (Figures 18 and 19), the formation of carbon dioxide increased almost uniformly with the filament current and then increased suddenly at the ignition amperage. When kerosene was used, the production of carbon dioxide increased gradually with the filament current.

Each of the knock suppressors, selenium diethyl, lead tetraethyl, lead tetramethyl (Figure 15), isopropyl iodide, *n*-butyl iodide (Figure 17), and the knock inducers, propyl nitrite, *n*-butyl nitrite, and isoamyl nitrite (Figure 16) were used with toluene. Lead tetraethyl, selenium diethyl (Figure 19), *n*-butyl iodide (Figure 18), and isoamyl nitrite (Figure 18) were used with isoamyl acetate, and lead tetraethyl (Figure 20) with kerosene.

Without exception, the addition of these knock suppressors to the fuels mentioned decreased the pre-ignition combustion as shown by the decrease in the carbon dioxide content of the gaseous combustion products from that present in similar products of the partial combustion of the fuels without the antiknock dopes. On the contrary, the addition of a knock inducer caused a marked increase in the pre-ignition combustion.

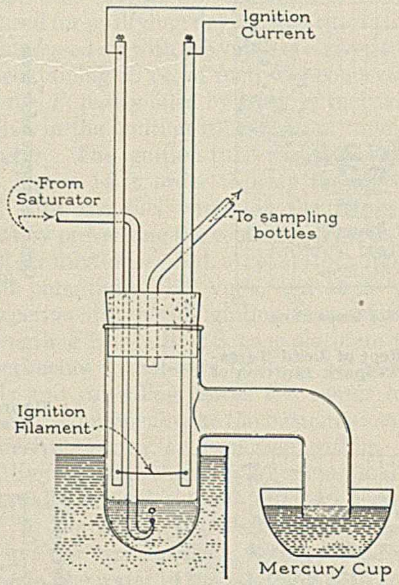

Figure 14—Final Design of Ignition Chamber Used in Measuring Pre-ignition Combustion

Besides curves (1), (2), (3), and (4) shown in Figure 18, three others were obtained by means of the same platinum filament. These, in the order determined, were for (5) isoamyl acetate, (6) isoamyl acetate containing approximately 1.95 per cent by volume of lead tetraethyl, and (7) pure isoamyl acetate. Curve (3) shows slightly less carbon dioxide formation than (1), curve (5) practically coincided with (1) from 3.0 to 3.8 amperes, while (7) coincided with (1) and (5) from 2.9 to 3.8 amperes and was slightly above (3) from 2.8 to 3.8 amperes. From Figure 20 it is apparent that the platinum filament, which had been used in the determination of pre-ignition combustion in kerosene-air mixtures containing lead tetraethyl, afterwards caused nearly as great a formation of carbon dioxide in undoped kerosene-air mixtures as it did when new. These results indicate that the decrease in pre-ignition combustion and increase in ignition temperature caused by the knock suppressor were not due to poisoning of the platinum filament by lead, iodine, or some other substance.

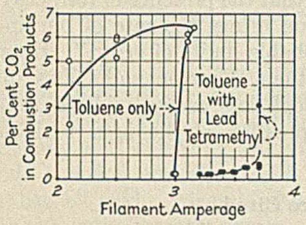

Figure 15—Effect of Lead Tetramethyl on Pre-ignition Combustion of Toluene. Saturator Temperature, 25° C.

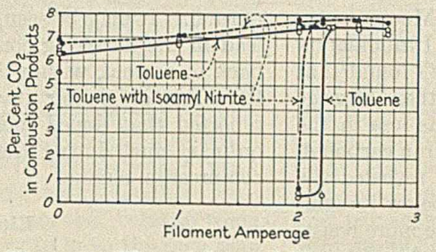

Figure 16—Effect of Isoamyl Nitrite on Pre-ignition Combustion of Toluene. Palladium Ignition Filament. Saturator Temperature, 25° C.

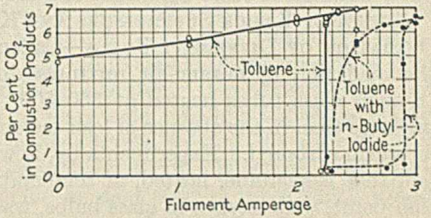

Figure 17—Effect of *n*-Butyl Iodide on Pre-ignition Combustion of Toluene. Palladium Ignition Filament. Saturator Temperature, 25° C.

At a saturator temperature of 25° C., toluene to which 1.95 per cent by volume of carbon tetrachloride had been added, gave fuel-air mixtures having an ignition amperage from 0.4 to 0.6 ampere higher than that for pure toluene. Pre-ignition combustion was also decreased markedly by the presence of this quantity of carbon tetrachloride. Probably differences in apparatus and experimental methods may account for the apparent disagreement between these results and the observations of Masson and Hamilton (*13*) who, by a modification of the Moore ignition meter, found that the auto-ignition temperatures of mixtures of benzene and carbon tetrachloride, containing up to 90 per cent of the latter, were lower than that for pure benzene.

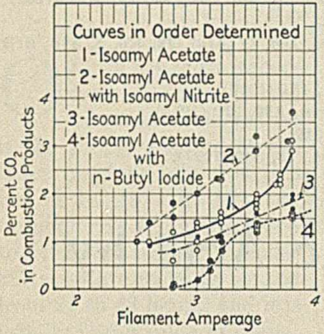

Figure 18—Effect of Isoamyl Nitrite and of *n*-Butyl Iodide on Pre-ignition Combustion of Isoamyl Acetate. Saturator Temperature, 46° C.

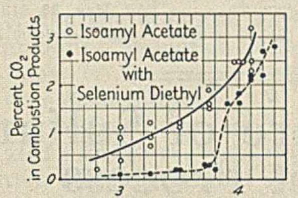

Figure 19—Effect of Selenium Diethyl on Pre-ignition Combustion of Isoamyl Acetate. Saturator Temperature, 50° C.

Discussion

Since the experiments described in this paper were begun, publications of a number of other investigators have appeared which show also that knock suppressors increase the ignition temperatures and hinder, or, in some cases, even inhibit the oxidation of certain fuels, while, on the contrary, knock inducers lower the ignition temperatures and increase or accelerate the oxidation.

Effect of Knock Suppressors and Knock Inducers on Ignition Temperatures—The observation by Ormandy and Craven (*15*) that the addition of 0.25 per cent of lead tetraethyl to *n*-heptane produced a drop of 14° C. in the ignition temperature as determined by a modified Moore ignition meter, is in apparent disagreement with the above view. It is to be noted, however, that the Moore meter does not permit accurate control of the composition of the fuel-air mixture under observation. The fuel-air mixture in contact with the heated surface of the ignition meter may vary from lean to the very rich depending upon diffusion and also upon the partial combustion taking place during the time interval after the drop of fuel makes contact with the surface of the meter until ignition occurs.

The hot-wire ignition curves obtained in the present work show that knock suppressors produce their least effect on the ignition amperages of mixtures with compositions near the limits of inflammability, and their greatest effect on the mixture which is ignited most easily. The addition of a knock suppressor to a fuel-air mixture richer than the one most easily ignited may produce an anomalous effect, such as, for example, the case indicated by Figure 2 in which the ignition amperage of toluene with lead tetraethyl is even 0.5 ampere less than for pure toluene at the saturator temperature of 30° C. The minimum of the curve for toluene containing the antiknock material, however, is at an amperage considerably higher than that for the pure toluene. In view of these observations, it is probable that the Moore meter would give different results, both as to ignition temperatures and to the effect of antiknock dopes on ignition temperatures, if the fuel-air ratio of mixtures used in the tests would be controlled accurately throughout the explosive interval. Knock suppressors and knock inducers would probably have greater effects on the mixtures near those of the composition to give complete combustion than on the lean or rich mixtures.

The dependence of the relative ease of ignition of fuel-air mixtures on the ratio of combustible liquid to air has evidently been considered by Thompson (*18*), who noted the character of ignition when different quantities of fuel were used, and then employed "what appeared to be the best quantity" for his determinations.

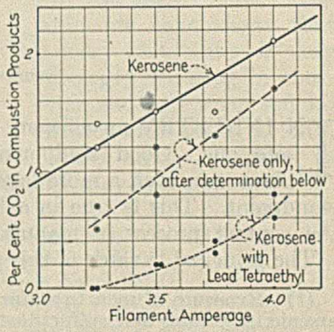

Figure 20—Effect of Lead Tetraethyl on Pre-ignition Combustion of Kerosene. Saturator Temperature, 80° C.

A more sensitive form of the Moore ignition meter than that used by Ormandy and Craven was employed by Masson and Hamilton (*13*), who found that additions of lead tetraethyl to *n*-heptane in the proportion of up to 10 cc. per gallon caused the auto-ignition temperature to increase from 450° C. for pure heptane to about 545° C. for the doped fuel. Gradually increasing additions of lead tetraethyl to alcohol caused a decrease in the ignition temperature, but with benzene the ignition temperature first decreased and later increased as the concentration of lead tetraethyl was increased. Tanaka and Nagai (*17*) noted that small amounts of selenium diethyl, lead tetraethyl, pyridine, or aromatic amines raised the spontaneous ignition temperatures of alcohols, but had little or no effect on those of methyl cyclohexane and ether. Later (*7*, *21*) compounds which have good antiknock effects were observed to increase the spontaneous ignition temperatures determined for a number of fuels by means of a modified Moore meter.

Effect of Knock Suppressors and Knock Inducers on Oxidation of Different Fuels—Callendar (*4*) found that the oxidation of hexane-air mixtures during their passage through glass tubes heated at 350–500° C. was less in the presence than in the absence of lead tetraethyl, iron carbonyl, or nickel carbonyl. Experiments by Lewis (*9*) revealed the fact that isopentane, heated, at temperatures below its ignition point, with oxygen in glass bulbs, was made more resistant to oxidation by the addition of 1 per cent of lead tetraethyl. Layng and Youker (*8*) observed that the slow oxidation of heptane in the gas phase at 160° C. was inhibited or prevented by 1 per cent of ethyl fluid. In similar experiments the oxidation of heptane was accelerated by 1 per cent of butyl nitrite. Bennett and Mardles (*1*, *12*) have likewise reported that lead tetraethyl and nickel carbonyl increase the ignition temperatures and inhibit the low temperature oxidations of hydrocarbons and other fuels.

Butkov (*3*) found that *n*-heptane in a bomb at 230° C. under a pressure of 3 atmospheres of oxygen yielded carbon dioxide six times more rapidly than did the same fuel to which 2 per cent of aniline had been added. Dumanois and Mondain-Monval (*5*) made somewhat similar experiments on pentane confined in a rotating, cylindrical steel bomb under an initial air pressure of 5.3 kg. above atmospheric and heated gradually from 20° to 300° C. Under these conditions the oxidation of pentane-air mixtures richer than that for complete combustion was inhibited by the presence of 0.11 per cent of lead tetraethyl. This small quantity of the knock suppressor increased the spontaneous ignition temperature by about 10° C.

By analyzing samples of gas withdrawn from an engine cylinder at various points in the explosion period by means of a special quick-acting, water-cooled sampling valve, Lovell and Coleman with Boyd (*10*) showed "that when the engine knocks, whether the detonation is caused by the presence of kerosene in the gasoline or by a chemical knock inducer (isopropyl nitrite), the gasoline burns at a rate more rapid than normal. It may be seen, also, that the presence of tetraethyl lead in the knocking combustion brings the rate of burning back to normal, within the probable limits of error." Upon the basis of similar investigations, Egerton and Gates (*6*) reported that doped fuel is much less easily oxidized than ordinary fuel during the compression stroke in a variable compression engine.

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Safety in the Manufacture of Sulfuric Acid by the Contact Process[1]

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IN INDUSTRY an efficient process is often a relatively safe one. Good equipment and proper maintenance place it in even a more favorable position from a safety standpoint. This is true in a large measure in the case of the contact process of manufacturing sulfuric acid.

The principal hazards of this process are:

(1) Exposure of men to sulfur dioxides, sulfuric acid fumes, arsenic, selenium, and sulfur dust.
(2) Possibility of sulfur dust explosions (preventable by wetting down while handling).
(3) Possibility of undermining sulfur stock piles with subsequent cave-ins on men.
(4) Ordinary machinery hazards in sulfur burner and blower rooms and where belts, pulleys, and gears are used to transmit power to pumps.
(5) Drips and sprays of acid from leaks in pipe lines and tanks.
(6) Acid flowing from broken gage glasses.
(7) Exposure to fumes and acid when men are required to work inside tanks, towers, and other apparatus.
(8) Hazards incident to the handling of heavy pieces of equipment when making repairs.

It is important that the men wear gas masks whenever exposed to concentrated sulfur dioxide and sulfuric acid fumes; also arsenic and selenium of only mild concentration as when treating the contact mass for the purpose of reviving. Respirators and goggles of good design will afford ample protection against sulfur dust. Reasonable care in shoveling sulfur from the piles will help to prevent men being injured by cave-ins. However, when working from large piles close supervision is necessary.

There is ample information available from many different sources on methods of safeguarding all ordinary machinery hazards. Drips and sprays of acid from leaks in pipe lines and tanks are preventable by good original installation work, careful supervision of operations, and avoidance of makeshift repair work. Only the best acid-resisting packing material in joints and valve glands and plenty of acid-resisting paint should be used to prevent external corrosion. Gage glasses should be used in acid tanks only if absolutely necessary. They should be regarded as extra hazardous and the best possible precaution taken against their breakage. They should be amply protected with stout guards. Water

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[1] Received May 1, 1929.

showers (commonly called safety showers) should be provided in ample number to enable a man splashed with acid to reach one conveniently from any position adjacent to the apparatus. They should be placed not more than 50 feet from any operating position in which a man might be splashed or sprayed with acid, and the man should not have to make more than one right-angle turn in his effort to reach one. The showers should be equipped with quick-opening valves and the sizes of the heads and riser pipes should be sufficient to deluge one with water.

Work inside tanks and apparatus requires the utmost precaution for safety. The tanks or apparatus should be thoroughly freed of all acid and fumes by thorough and repeated washing and steaming, winding up by filling with a weak soda solution and allowing it to stand long enough to neutralize all acid. All mud should be removed, because when stirred up it liberates fumes. It pays to have the men who enter protect themselves with gas masks and safety belts. The belts are used with life lines attached so that quick rescue can be made from outside the tanks or apparatus if anything goes wrong. Attendants should always be stationed at the tank manholes while men are inside. Each acid pipe line leading to the tank should have a section removed and the end blanked off so there can be no possibility of acid entering while the men are at work.

Ample provision should be made for the handling of heavy parts in time of repairs. Much can be done to facilitate this in the original design of the buildings by providing anchorage of sufficient strength for hoists and by including large doorways and floor openings. The latter should be protected with railings and toe-boards.

In general, it is well to make all parts of the apparatus easily accessible by the provision of good permanent walkways and stairways. Stairways should be provided in preference to ladders in so far as possible. It is always good from a safety standpoint to place acid pipe-line valves not more than 18 inches above floor levels, so that the operator can keep his face well away from them. However, all important passageways should be kept clear of pipes which would form stumbling hazards.

Floors should be of acid-resisting material and sloped to drain well to sewers or pumps. Ample water hose and outlets should be available for washing away spills of acid.

Adequate ventilation is always important in buildings housing acid processes and is usually obtained by roof monitors supplemented with wall openings at the ground level to provide the necessary circulation of air.

Effect of Nitrate Oxygen upon Tannery Effluent[1]

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The reduction of nitrate in the presence of oxidizable organic material has been studied and the following facts have been noted: (*a*) the amount and composition of the gas produced during the reduction; (*b*) the amount of reduction taking place under various conditions; (*c*) the gas pressure attained during the reduction of the nitrate.

It is shown that large amounts of nitrogen are liberated through the reduction of nitrate by bacterial action and it is pointed out that this nitrogen may be derived from several sources. During the early stages of the reduction considerable carbon dioxide is produced, indicating that the carbonaceous material is acted upon most readily. At a later period it appears that the sulfur compounds are oxidized by the nitrate.

ONE of the most important processes in the manufacture of leather is the proper soaking of the hides or skins, and for this reason large amounts of tannery soak water are passed to rivers and streams. Hides and skins are generally soaked from 24 to 48 hours, and it is usually found upon examination that the resulting soak water contains no dissolved oxygen—in bacteriological parlance, the water is strictly anaerobic. The effluent from a 48-hour soak may contain upward of 300 million bacteria per milliliter of soak water, and for this reason the oxygen requirement of the water is extremely high. Many workers have studied the effect of nitrate oxygen upon sewage in general, but apparently little has been done with regard to tannery effluent.

Urbain (*4*) has pointed out that it is necessary for anaerobic conditions to exist before nitrate oxygen can be utilized by bacteria. The present writers have found this contention to be in accordance with their experimental work. However, in utilizing tannery soak water, the effluent is practically free from dissolved oxygen and is consequently anaerobic. Many bacteria have been found which are capable of reducing nitrates to nitrites. Buchanan and Fulmer (*1*) point out that most of these bacteria are strictly aerobes except when able to reduce nitrates and nitrites. These bacteria are proteolytic and unable to act upon carbohydrates except in the presence of nitrates. Buchanan and Fulmer further point out that the oxygen secured through reduction of nitrates and nitrites is available to the organism quite as readily as atmospheric oxygen. The reduction of nitrate with subsequent oxidation of sulfur liberates energy for bacterial use. Experiments have shown that tannery soak water is very strongly reducing in character and acts upon sodium nitrate with great avidity, giving a variety of products. When nitrate is added to these waters, the following reactions may be visualized:

$$(NO_3)^- + 2H^+ + 2\epsilon \longrightarrow (NO_2)^- + H_2O$$
$$NO_2 + 2H^+ + 2\epsilon \longrightarrow NO + H_2O$$
$$2NO + 4H^+ + 4\epsilon \longrightarrow N_2 + 2H_2O$$
$$NO + 5H^+ + 5\epsilon \longrightarrow NH_3 + H_2O$$
$$NH_3 + HNO_2 \longrightarrow NH_4NO_2 \longrightarrow N_2 + 2H_2O$$

In determining the biochemical oxygen demand by the nitrate method it is usual to estimate the residual nitrate and nitrite in the incubated solution. The writers believe that this leads to erroneous interpretation, because it appears that more of the nitrogen cycle should be estimated. Theis and McMillen (*3*) showed that on treating tannery soak water with standard solutions of sodium nitrate large amounts of the nitrate were consumed. Table I gives a summary of the data. This table shows that comparatively large amounts of nitrate are consumed but only small amounts accounted for in the usual analysis. Buswell (*2*) points out the conflicting evi-

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[1] Received April 6, 1929. Presented before the Division of Water, Sewage, and Sanitation Chemistry at the 77th Meeting of the American Chemical Society, Columbus, Ohio, April 29 to May 3, 1929.

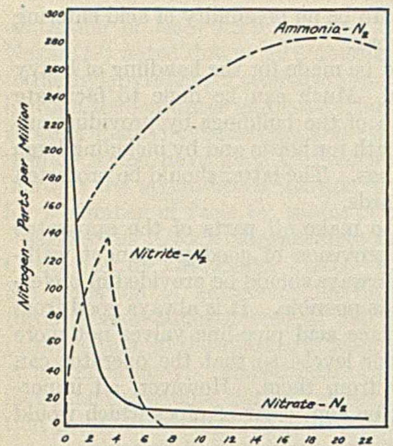

Figure 1—Reduction of Nitrate, When 230 p. p. m. Are Added

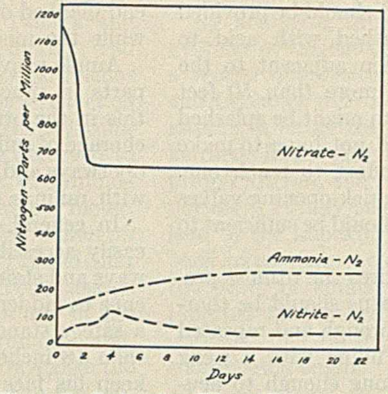

Figure 2—Reduction When 1200 p. p. m. of Nitrate Are Added

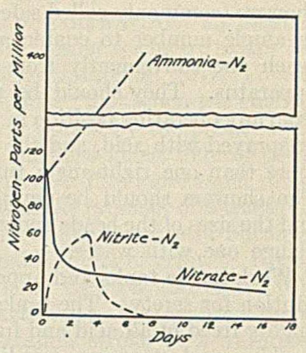

Figure 3—Reduction When 100 p. p. m. of Nitrate Are Added

dence existing with regard to the evolution of nitrogen gas through the reduction of nitrate by sewage. The experiences of the writers have indicated that large amounts of gas are formed through this reduction and for this reason the following experimental work was undertaken.

Table I—Nitrate Reduction by Soak Waters

	Period of Soak			
	24 Hours	48 Hours	96 Hours	120 Hours
	P. p. m.	*P. p. m.*	*P. p. m.*	*P. p. m.*
Nitrate nitrogen reduced	1550.0	1670.0	3150.0	8800.0
Nitrite nitrogen formed	1.4	200.0	280.0	2100.0
Ammonia nitrogen formed	42.0	32.6	22.0	67.5

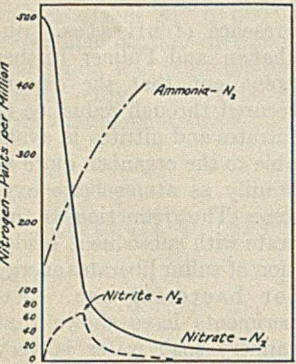

Figure 4—Reduction When 500 p. p. m. of Nitrate Are Added

Experimental Procedure

Series 1—The soak water was prepared by soaking heavy steer hides in water for 96 hours at 25° C. Fifteen hundred milliliters of this prepared water were placed in a 2000-ml. bottle and this solution in turn was treated with standard nitrate solution. The space above the solution was flushed completely with nitrogen gas in order to keep the solutions anaerobic. The bottles were shaken once daily and samples withdrawn for estimation of nitrate, nitrite, and ammonia. These samples were withdrawn in an atmosphere of nitrogen and only nitrogen gas came in contact with the solutions in question. Figures 1 to 5 show the experimental data obtained under these conditions.

Series 2—In another series of experiments 100 ml. of the same soak water were placed in 200-ml. bottles together with varying amounts of standard nitrate solution. These bottles in turn were fitted with mercury manometers and placed in a thermostat maintained at 37.5° C. Pressures were recorded several times daily. Runs were also made similarly at 25° C. Figures 6 to 8 give in graphical form the experimental results of this work.

Series 3—In this series of experiments 1500 ml. of solution as made in Series 1 were connected directly to a gas analysis apparatus and each 100 ml. of gas evolved was analyzed for carbon dioxide, oxygen, and nitrogen. A complete analysis of the evolved gas showed only these three gases to be present and in all subsequent work only these were determined. Figure 9 shows the type of apparatus used and Figures 10 and 11 show the analytical data obtained.

Discussion

From Figures 1 to 5 it is readily seen that when using 110 p. p. m. of nitrate nitrogen most of the nitrate is reduced within 24 hours; the nitrite nitrogen reaches a maximum the third day and then decreases sharply to practically zero; the ammonia increases abruptly, rising to 400 per cent in 7 days. When using 500 p. p. m. of nitrate nitrogen, it requires nearly 7 days to bring the nitrate reduction to a practical equilibrium. The ammonia again shows a sharp rise. When 2500 p. p. m. of nitrate are used, an entirely different picture results. For 7 days no reduction of nitrate occurs, but after this latent period a rapid reduction takes place which does not attain equilibrium in 30 days.

When small amounts of nitrate are used as illustrated by Figures 1 and 2, equilibrium is attained at a very early period. In the early stages of reduction much gas is formed, sufficient in most cases to expel the stoppers from the bottles. This generation of gas continues until about the time that the nitrite formation ceases. It is also during this period that ammonia formation begins. It is quite possible that a part of the gas formed during the early stages is due to the interaction of nitrite and ammonia to form ammonium nitrite, which by autoxidation yields molecular nitrogen.

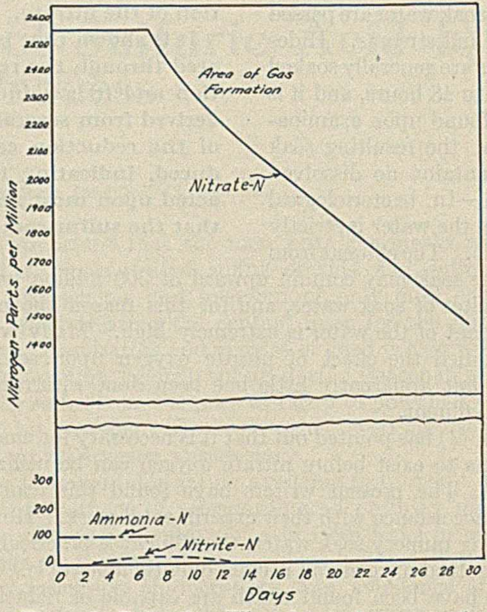

Figure 5—Reduction When Large Amounts of Nitrate Are Added

$$NH_4NO_2 \longrightarrow N_2 + 2H_2O$$

This suggestion is further strengthened by the fact that if the bottles are shaken violently for a few minutes the gas pressure increases very greatly.

When large amounts of nitrate are used, as illustrated in Figure 5, other factors enter into the reaction. For a certain period of time there is apparently no reaction, the nitrate is not reduced, practically no nitrite is formed, and no gas is evolved. After this lag period (in Figure 5 about 7 days) there is a rapid reduction of the nitrate and a copious evolution of gas, but there is no apparent equilibrium at the end of about 30 days. It appears that in the initial stages the large amount of nitrate present acts as an antiseptic and thus hinders the reaction. This antiseptic action is finally broken down and the bacteria become acclimated to this environment, and it is at this stage that rapid reduction takes place.

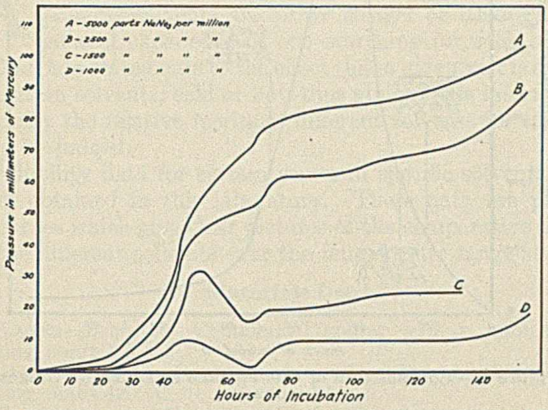

Figure 6—Pressure Developed during Incubation at 25° C. in an Atmosphere of Nitrogen Gas

The solutions to which were added small amounts of nitrate, though having attained an equilibrium and still generating some gas, showed that the oxygen demand had not been satisfied. These solutions had a putrid odor of volatile sulfides. The solutions to which 1000 p. p. m. of nitrate had been added showed that their oxygen demand had been practically satisfied.

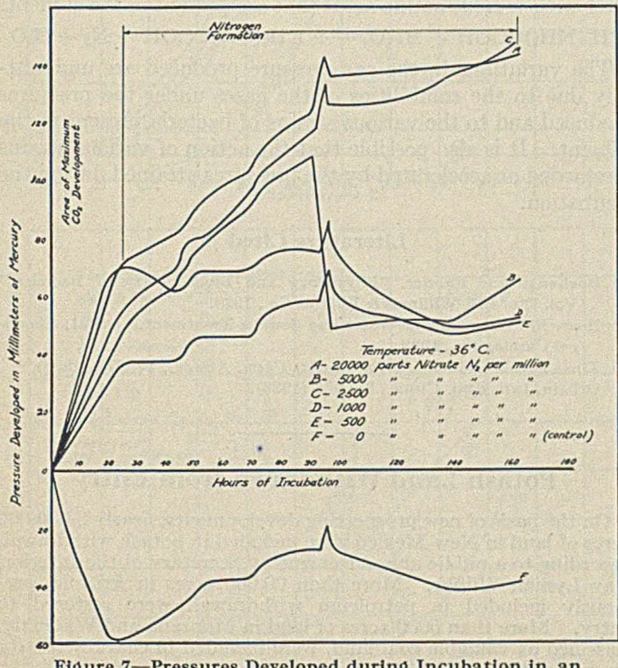

Figure 7—Pressures Developed during Incubation in an Atmosphere of Air

In reduction of nitrate to nitrite, energy to the amount of 10,000 gram-calories would have to be added for each gram-molecule of nitrate consumed. The nitrites are more readily utilizable than the nitrates, which may explain to some degree why they do not show up strongly on analysis.

The nature of the gases found, through the simultaneous interaction of the nitrate and sewage, opened up a very interesting field of investigation. Table II and Figures 10 and 11 show the data taken.

Table II—Amount and Composition of Evolved Gases

Period of Incubation	Gas Evolved	Nitrogen Evolved	Analysis		
			CO_2	O_2	N_2
Hours	*Ml.*	*Ml.*	%	%	%
20	86.3	69.0	9.65	10.5	79.85
24	170.6	140.0	8.75	6.9	84.40
26	256.7	216.0	8.00	3.2	88.80
43	959.5	895.0	2.00	0.5	97.50
49	1141.0	1137.0	1.79	0.0	98.21

From Table II it is readily seen that the available free oxygen is rapidly consumed whereas the carbon dioxide increases to a maximum and then decreases rapidly. On the other hand, the nitrogen percentage increases constantly.

Figure 10 shows the volume of gas produced when tannery effluent is treated with varying amounts of nitrate oxygen. Using 1000 to 5000 p. p. m., the volume of the gas increases to a maximum within 96 hours and then rapidly decreases. Using a small concentration of nitrate (200 p. p. m.), the volume of gas reaches a peak value within 48 hours and then also decreases. Analysis of the gas produced at different intervals showed that carbon dioxide is produced in the early stages but decreases in the later stages of the reaction. The nitrogen continually increases similarly to data given in Table II and Figure 11. The above data show conclusively that much nitrogen gas is formed during this reduction.

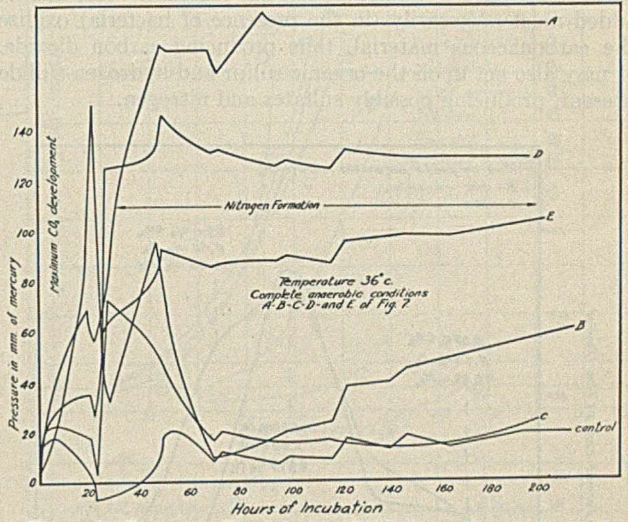

Figure 8—Pressures Developed at 36° C. in an Atmosphere of Nitrogen Gas

Figures 6, 7, and 8 show pressures attained when tannery soak water is treated with nitrate oxygen. As will be seen, regardless of the concentration of the nitrate used, the pressure curves increase gradually and after a certain period of incubation attain either a maximum or a point of inflection. In the high concentrations, showing a point of inflection, the pressure curve then continues to rise but with no apparent equilibrium. In the lower concentrations the pressure curve always exhibits a maximum point, decreases, and then usually rises to a new maximum and may even repeat. Figure 6 shows the pressure curve for incubation at 25° C. The first sharp break in the curve occurs at about 48 hours. Incubation at 36° C., as shown in Figure 7, shows the first distinct discontinuity at about 25 hours. This difference would be expected in view of the temperature conditions. An atmosphere of air was used for the data in Figure 7, while in Figure 8 an atmosphere of nitrogen was used.

A high concentration of nitrate always gave a "sweet" water and no sulfide odor, but a nitrate concentration of 1000 p. p. m. or less gave invariably a putrid water with a very strong sulfide odor, showing that the oxygen demand of the water had not been satisfied.

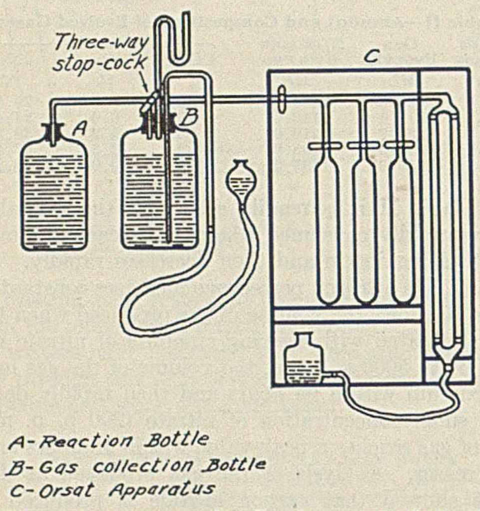

Figure 9—Apparatus for Continuous Analysis of Gases Developed

In view of the complexity of the dissolved substances in tannery effluent, it is not easy to account for the extreme variations in gas composition and gas pressure. The nitrate added must necessarily (in the presence of bacteria) oxidize the carbonaceous material, thus producing carbon dioxide. It may also act upon the organic sulfur and hydrogen sulfide present, producing possibly sulfates and nitrogen.

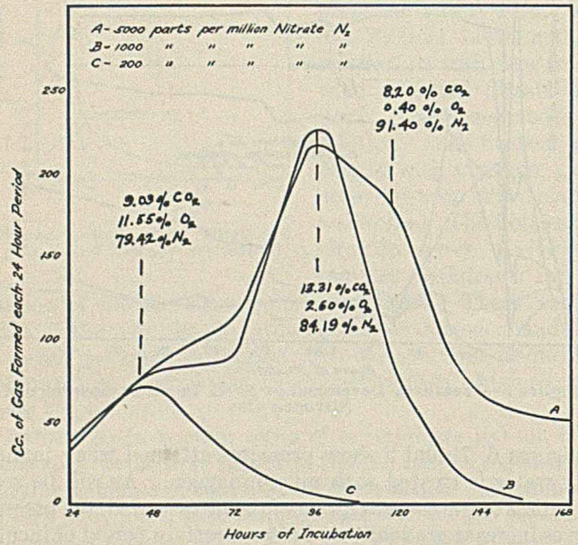

Figure 10—Amount and Composition of Evolved Gases, Using Varying Amounts of Nitrate

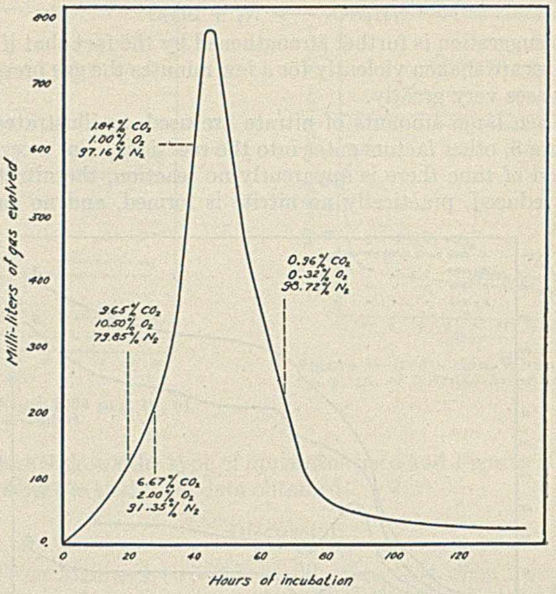

Figure 11—Composition of Gas Formed at Different Stages of Incubation

It is well known that through bacterial action in the presence of nitrates and sulfur compounds an oxidation of the sulfur occurs with corresponding reduction of the nitrate. This may be illustrated by the following equation:

$$6KNO_3 + 5S + 2H_2O \longrightarrow 3K_2SO_4 + 2H_2SO_4 + 3N_2$$

The reduction of nitrate with accompanying oxidation of sulfur is supposed to liberate energy for bacterial utilization. Another possible reaction appears to be:

$$8KNO_3 + 5H_2S \longrightarrow 4K_2SO_4 + H_2SO_4 + 4H_2O + 4N_2$$

This reaction would also liberate energy for bacterial use. It is well known that sulfur compounds are present in tannery soak water and are derived from the decomposition of the amino acid, cystine. Cystine may then break down, giving the simpler substance, hydrogen sulfide. The above reactions may account, at least to some extent, for the liberation of molecular nitrogen.

Analysis of the gas has also shown high percentages of carbon dioxide, and this undoubtedly is derived from the oxidation of carbonaceous matter by the nitrate, as illustrated:

$$5C_6H_{12}O_6 + 24HNO_3 \longrightarrow 30CO_2 + 42H_2O + 12N_2$$

It is also possible that during oxidation various oxides of nitrogen may appear. As shown earlier in this paper, the nitrate is reduced to nitrite and this nitrite in turn may react with various amino acids that are present in the effluent.

$$CH_2(NH_2)COOH + HNO_2 \longrightarrow CH_2(OH)COOH + N_2 + H_2O$$

The variations in the gas pressure produced are undoubtedly due to the solubilities of the gases under the pressures produced and to the various strains of bacteria present in the effluent. It is also possible that the action of various strains is retarded or accelerated by the pressures attained during the incubation.

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Potash Land Withdrawn from Entry

On the basis of new prospecting developments, nearly 2,000,000 acres of land in New Mexico were included in potash withdrawal, according to a public announcement by Secretary of the Interior, Ray Lyman Wilbur. More than 90,000 acres in Arizona, previously included in petroleum withdrawal, were restored to entry. More than 5000 acres of land in Montana and Wyoming, classified as valuable coal land, were included in coal reserve for the use of the United States.

Solvents for Waxes[1]

O. A. Pickett

Experimental Station, Hercules Powder Company, Kenvil, N. J.

Available data on the solubility of waxes in various possible solvents are either meager or lacking. The general experience of one searching for such data is to find only statements to the effect that a given wax is soluble in certain solvents, cold or hot, thus giving little information whereby the relative merits of different solvents for the wax may be judged.

Solubility data for certain waxes in specific solvents have been obtained in this laboratory. These data are plotted to curves which give clear pictures of the comparative values of the different solvents over the temperature range studied.

Materials Used

Waxes—*Beeswax.* Commercial grade; yellow, unbleached; setting point 62° C.

Candelilla wax. Commercial grade; light yellow color; setting point 66° C.

Carnauba wax. Commercial grade; light gray color with slight greenish tint; setting point 82° C.

Montan wax. Commercial grade; dark brown color; setting point 69° C.

Solvents—(1) *V. M. & P. Naphtha.* Standard grade petroleum hydrocarbons.

(2) *Turpentine.* Standard steam-distilled wood turpentine.

(3) *No. 22 Thinner.* Industrial solvent carrying approximately 55 per cent terpene hydrocarbons and 45 per cent gasoline.

(4) *Solvenol.* Industrial solvent consisting of approximately 97 per cent terpene hydrocarbons and 3 per cent saturated hydrocarbons.

(5) *Pine oil.* Standard grade of Yarmor pine oil.

(6) *Sulfonated castor oil.* Industrial grade carrying 1.46 per cent total sulfur equivalent to 3.65 per cent SO_3.

(7) *Equal parts, by weight, of pine oil (5) and sulfonated castor oil (6).* Such mixtures are finding extensive use as a substitute for straight sulfonated castor oil in the textile industry for dewaxing fibers.

Specific gravity and boiling range data for the several solvents used appear in Table I.

Table I—Specific Gravity and Boiling Range Data for Solvents

	V. M. & P. Naphtha (1)	Steam-Distilled Turpentine (2)	No. 22 Thinner (3)	Solvenol (4)	Pine Oil (5)
Sp. gr. 15.6°/15.6° C.	0.750	0.860	0.820	0.857	0.935
		Boiling range[a]			
Per cent	° *C.*	° *C.*	° *C.*	° *C.*	° *C.*
5	100	159.8	155	172	194
10	104	160.3	156	174	199
20	110.5	160.8	157	176	204
30	115.5	161.4	158	...	206
40	121	161.9	159	...	208
50	126	162.5	160	178	210
60	132	163.2	162	...	212
70	139	164.2	164	...	213
80	149	165.9	166	...	214
90	162	169.9	171	182	217
95	174	...	177	187	225

[a] Obtained according to A. S. T. M. turpentine boiling range specifications.

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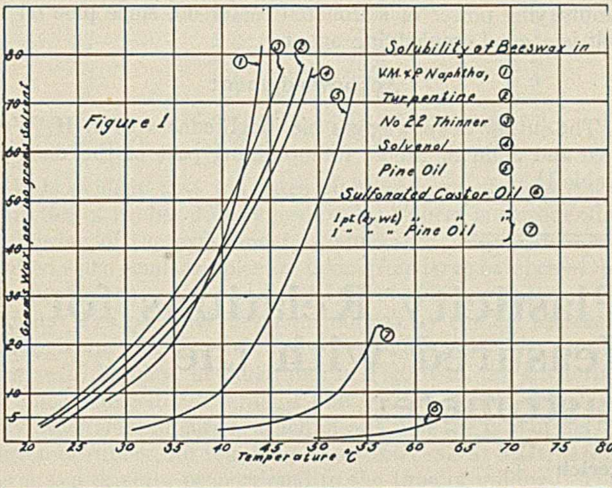
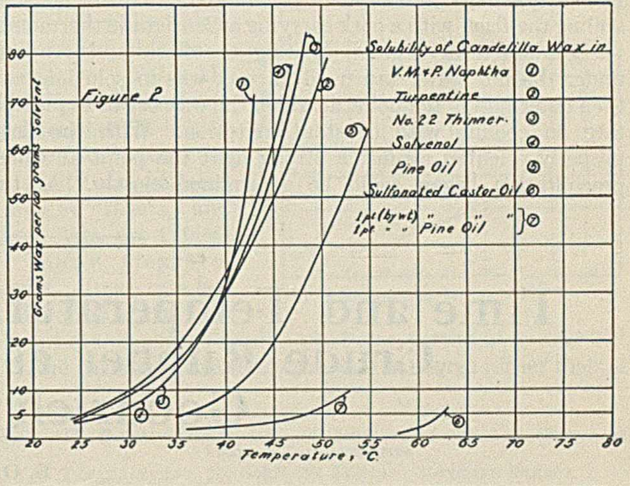
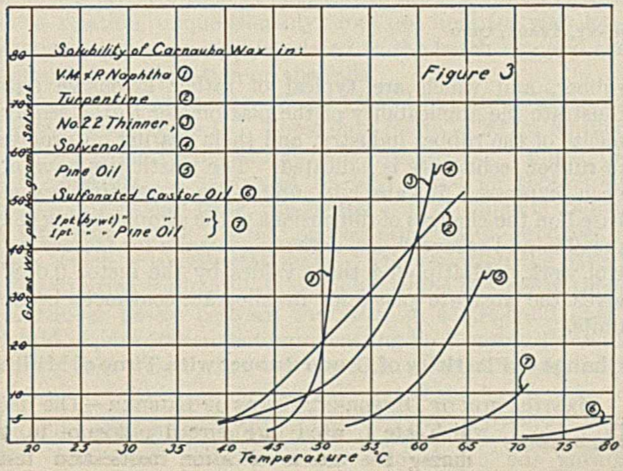
[1] Received March 29, 1929.







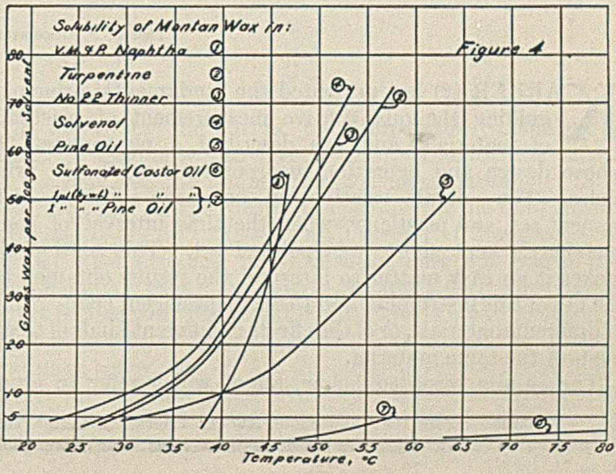


Table II—Solubility Data

A1-457-7.

Grams Wax per 100 gms. Solvent	V. M. & P. Naphtha				Turpentine				No. 22 Thinner				Solvenol				Pine Oil				Sulfonated Castor Oil				3 pt. Sulf. Cast. Oil 1 pt. Pine Oil			
	Beeswax	Candelilla	Carnauba	Montan	Beeswax	Candelilla	Carnauba	Montan	Beeswax	Candelilla	Carnauba	Montan	Beeswax	Candelilla	Carnauba	Montan	Beeswax	Candelilla	Carnauba	Montan	Beeswax	Candelilla	Carnauba	Montan	Beeswax	Candelilla	Carnauba	Montan
	Temperature, °C., of Saturation for grams Wax per 100 grams Solvent																											
1																					50		72	65				44
1.25																					52							
1.50																											63	
2																						60	75	80		37		52
2.5																					60				41			
3			45.5																				78				65	
4																						62				48		
5	25		47	39	23	26	41	29	22	28	42	28	24.5	26	42	23.5	35	36	55	31					47			
6																										50		
7.5																											69	
10	29	33	49	40	27	31	45	34	26	33	49	33	28	30.5	49.5	30	40	41	58.5	40					52			
15																				45								
20	35	37		42.5	32	37	49.5	40	31	37	55	39	33	35.5	55	38	43	45	62.5	48					55			
30				44	36	40	54	43	36		57	42	37.5	39	57	41	46	47	65.5	53								
32	38																											
40	40	41	51	45.5	40		59	46.5	38	42	59	46		41	59	44	48	50		58								
50		42			43	45	64	50		44	61	48	44	43		47	50	52		63								
60	42.5								43			56		45		50	51.5	54										
70					47	49		56.5	45	47			48	46		52.5	53											
80	44									48																		

Method of Making Tests

Solubility tests were made by weighing into a 100-cc. Erlenmeyer flask the desired amounts of wax and solvent, sealing the flask with a cork carrying a Centigrade thermometer graduated in degrees, heating the flask and contents under the hot water tap until all wax was in solution, and then determining the point at which the wax began to precipitate on cooling with constant agitation. With the flask properly oriented against a strong light the point at which precipitation began could be determined closely. At the lower temperatures this point could be checked consistently to within ±0.5° C., while at the higher temperatures it could be checked consistently to ±0.25° C.

The saturation points, of course, are for the least soluble components of the waxes in the solvents used. However, it was observed that once precipitation had set in it increased rapidly with further decrease in temperature.

Data and Discussion

The solubility data are given in Table II and Figures 1 to 4. It is evident that solubility curves (1), (2), (3), and (4) all lie relatively close together, with (5) somewhat lower. At lower temperatures Solvenol, No. 22 Thinner, and turpentine are all better solvents for the waxes tested than V. M. & P. naphtha, while at the higher temperatures the latter is the best solvent.

Curves marked (6) show that sulfonated castor oil is a relatively poor solvent for the waxes. Yet it is known to be a good emulsifying agent in the dewaxing of textile fibers. Mixtures of pine oil and sulfonated castor oil are coming into extensive use for such purposes; curves marked (7) partly explain why such mixtures are increasing in favor. The addition of pine oil increases the solubility of the wax without appreciably decreasing the emulsifying power of sulfonated castor oil, since pine oil itself is a good emulsifying agent.

Acknowledgment

The author acknowledges his indebtedness to J. H. Wallace and John S. Moore for obtaining part of the data in Table II.

Time and Temperature-Plasticity Relations for Crude Rubber as Measured with the Goodrich Plastometer[1]

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Karrer (*2*) has presented the fundamental principles guiding the quantitative measurement of plasticity of materials, and has described a plastometer (*1*) whose design and operation incorporate these basic principles. The simple relationship between softness, permanent set, and plasticity, when the time interval of compression is kept short, was pointed out. This relationship makes it an easy matter to interpret the results obtained by the use of this instrument and to make intelligent comparisons of different materials, or of the effects of different kinds of treatment of the same material.

The results recorded below, all of which refer to crude rubber, and which are typical of rather extensive data, illustrate the applicability of the plastometer to the requirements of the rubber industry, and their bearing on progress in rubber technology is indicated. The plasticities have not been expressed in absolute units, since relative values, based on the changes of dimensions of the sample during compression and recovery, are entirely adequate for factory control work. Multiplying these values by the factor 0.01876 gives the absolute plasticity in kilogram-centimeter-second units.

Change of Plasticity of Crude Rubber with Time of Milling

Mastication of Different Kinds of Rubber—The data in Table I, which are plotted in Figure 1*a*, were obtained during the course of some mastication tests and refer

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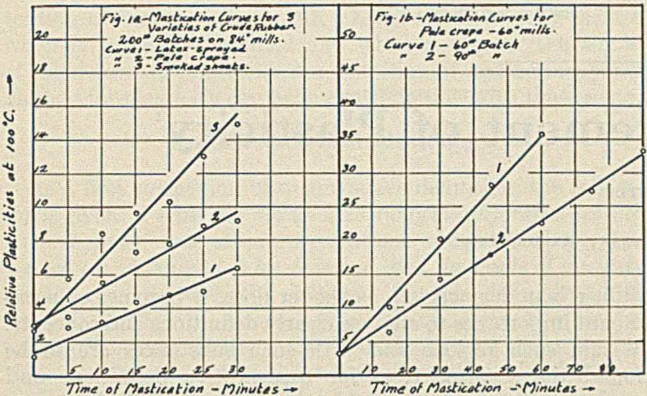
[1] Presented before the Division of Rubber Chemistry at the 76th Meeting of the American Chemical Society, Swampscott, Mass., September 10 to 14, 1928.

to 200-pound (91-kg.) batches milled on a 24 by 84 inch (61 by 213 cm.) smooth roll mill. The mill roll setting was kept constant at $^{9}/_{32}$ inch (7 mm.) and the cooling water regulated to give the same rate of temperature rise in each batch so that milling conditions might be as nearly as possible alike for all batches. Comparisons were made of pale crepe, smoked sheets, and latex-sprayed rubbers.



Unless stated otherwise, all measurements were made at 100° C. and, whatever the temperature, the samples were preheated for 20 minutes before they were put into the plastometer.

Table I—Relative Plasticities at 100° C. of Different Kinds of Rubber for Various Periods of Mastication

TIME OF MASTICATION	PALE CREPE	SMOKED SHEETS NO. 1	LATEX-SPRAYED NO. 1
Minutes			
0	2.9	2.7	1.1
5	3.4	5.7	2.8
10	5.5	8.3	3.1
15	7.3	9.6	4.3
20	7.7	10.2	4.7
25	8.8	13.0	4.9
30	9.1	14.9	6.3
Final batch temperature	227° F. (109° C.)	227° F. (109° C.)	233° F. (112° C.)

It is evident that the rates of breakdown of these three varieties of rubber differ enormously. There is considerable scattering of the experimental values, but this is to be expected when small samples are taken from large batches—i. e., the deviations are due to variations in different parts of the batch. The personal factor introduced by cutting the bank through the mill also influences the regularity of the results. For small batches, as illustrated in Figure 1*b*, the scattering is much reduced. A straight line fits the points as well as any other smooth curve, which means that the rate of mastication of rubber, for relatively short intervals at least, is uniform and directly proportional to the time of milling. This linear relation, unquestionably, does not hold for very long masticating periods, and is related to the batch size and the method of manipulation on the rolls.

EFFECT OF BATCH SIZE—Some typical results are shown in Table II and Figure 1*b*. These data relate to 20 by 60 inch (51 by 152 cm.) smooth roll mills operated at $^{1}/_{8}$-inch (3-mm.) opening. A 60-pound (27-kg.) batch on these rolls gives a fairly small bank, the greater part of which is rolling. A 90-pound (41-kg.) batch, on the other hand, produces a bank which is largely stationary. Theoretically, the extent of mastication is directly proportional to the number of times the rubber passes between the rolls, so a 90-pound batch should require 50 per cent more cutting back and forth and a 50 per cent longer time on the rolls to reach a plasticity equivalent to that attained by a 60-pound batch at any given time. This is verified to a satisfactory degree by the experimental data, the final plasticity of the 90-pound batch being practically equal, in 90 minutes, to that of a 60-pound batch at the end of 60 minutes, the former having been cut through the mill 50 per cent oftener.

Table II—Relative Plasticities of Pale Crepe at 100° C. in Different Batch Sizes for Various Periods of Mastication

TIME OF MASTICATION	60-LB. (27-KG.) BATCH	90-LB. (41-KG.) BATCH
Minutes		
0	3.3	3.3
15	10.1	6.2
30	20.3	14.1
45	28.2	17.8
60	35.7	22.4
75		27.1
90		33.5

A satisfactory linear relationship between plasticity and period of mastication is again observed in this case, although the latter is $1^{1}/_{2}$ hours. In fact, we have noted this proportionality for milling times as long as 2 hours. Such a simple relationship between milling time and plasticity does not hold for any other type of plastometer, and the ease of calculating milling time in terms of equivalent plasticities is clearly evident.

Temperature Coefficient of Plasticity

References in the literature to the effect of temperature upon the properties of rubber leave the impression that in the neighborhood of 70° C. the plasticity undergoes a sudden change and that above this temperature rubber is, in fact, a different material in this respect than it is at lower temperatures. Thus, Van Rossem and Van der Meyden (*3*) speak of rubber as being "fully plastic" at 70° C., but only "partially plastic" below this temperature. Table III and Figure 2 illustrate the manner in which temperature affects the plasticity of masticated smoked sheets, and these data are typical of many measurements. In no case has a discontinuity, or abrupt change, been found in plastic properties at or near 70° C.; the variation with temperature is of degree rather than of kind.

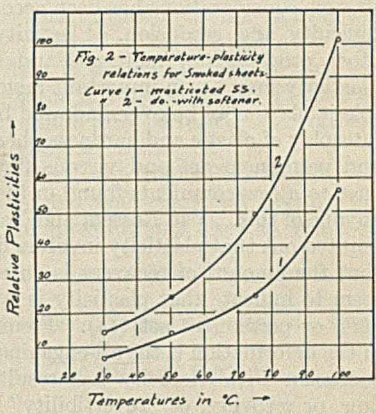


Table III—Relative Plasticities of Masticated Smoked Sheets at Various Temperatures

TEMPERATURE	NO SOFTENER ADDED	SOFTENER ADDED
° C.		
30	6.4	14.0
50	14.1	24.3
75	24.9	49.0
100	56.2	101.0

As shown by the curves, the temperature coefficient of plasticity gradually increases as the temperature is raised. In the first case the temperature coefficients are found to be 0.35, 0.75, and 1.50 per degree Centigrade for the temperature intervals of 30–40°, 70–80°, and 90–100° C., respectively. In the other instance, in which a softener was added, the corresponding values are 0.42, 1.50, and 2.45. This change in the temperature coefficient of plasticity is a confirmation of the desirability of low-temperature mastication, for at temperatures below, say, 60° C., the internal stresses set up in the rubber are high and rapid breakdown occurs, while at higher temperatures the internal resistance to deformation rapidly decreases, and little permanent softening of the rubber results.

The instrument has proved a powerful tool in the study of mastication, mixing, calendering, and tubing problems, some of the results of which, it is hoped, will be published in the near future. In speed and simplicity of operation it leaves little to be desired. The fact that the true plasticities, as measured with the instrument, are directly proportional to the figures which express them—a plasticity of 20, for example, indicates a material which is exactly twice as plastic as one for which the figure is 10—makes it possible to set up a convenient scale which is easily understood by machine operators with no technical training. This is of immense importance in factory control and can be accomplished at the present time by no other plastometer.

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Meaning and Measurement of Plasticity[1]

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ALTHOUGH the word "plasticity" is widely used in the arts and sciences, it has no definite quantitative meaning (*6*, *7*), yet the plastic properties of matter are of enormous importance in many industries. As scientific study of materials has increased, it has become more and more desirable to attain to a clearer idea of what is involved in this concept, to the end that plasticity may ultimately be quantitatively defined and measured.

The emergence of the word from common usage into the realm of technical words with well-defined meaning for quantitative considerations has been accompanied by considerable difficulty and confusion. Plasticity does closely relate to other properties of materials and the phenomena wherein plasticity may be an important factor are so varied that the role it plays may be overshadowed by and confused with the interplay of elastic and hardness phenomena on the one hand, and permanent set and viscous flow on the other. Reference to a few comments found in the literature will convince anyone of this. Van Rossem and Van der Meyden (*14*) have pointed out that plasticity involves more than deformation—that the amount of recovery is an essential element. Some seem to indicate that plasticity is synonymous with softness (*11*), or permanent set (*14*). Frequently the flow involved in the deformation is the all-engaging aspect and considerable confusion with viscosity has resulted (*1*, *2*, *16*). Inverse flow, or recovery, or "revertibility" is also to be considered. Loose and contradictory usage of the term exists in the rubber industry (*12*, *14*, *15*). A few attempt to use the term with the usual common-sensical meaning (*5*, *8*).

It does not help matters much to call plastic strain or plastic flow one of the three types of strains which are referred to as elastic, plastic, and pseudo-elastic (*3*). When the element of time is considered, all three of these classes merge into one another, since in the first there is quick and complete recovery, in the second no recovery, in the last slow recovery. The amount of deformation effected by a given force per unit area may have any value. The retention of the deformation may take place to any extent. Recovery may occur from perfectly complete to none; and from instantaneous to grossly and indefinitely slow. Whenever any property of matter, such as plasticity, that involves any of these factors is to be defined and measured, the quantitative definitions, the units, and the methods of measurement must allow for a gradation of the property from practically nil to an indefinitely great amount. Therefore, boundaries such as these for classification are difficult to set up and must remain diffuse. When a substance lies within the diffuse boundary region, as rubber does, it becomes of paramount importance to analyze clearly definitions and concepts. Within such regions and with such substances are to be found the severest tests for quantitative definitions and methods of measurement.

It is desirable to consider plasticity as an integral property of material and to base the quantitative definition and units and methods of measurement upon the integrated aspect of the phenomena involved in this property just as is done in practice in respect to viscosity and many other complex properties of materials. It is purposed to attempt this for plasticity if for no other reason than that it is extremely desirable to come to a clear and universal understanding regarding the definitions of certain mechanical properties of materials such as plasticity, softness, hardness, and permanent set, so that the concepts may become more serviceable and such properties be better controlled in the arts and industries.

Preliminary Definition

As an introductory and general definition more suited to the present purpose may be given this: *Plasticity is the susceptibility to and the retentivity of deformation.* The first aspect of plasticity refers to softness, the second to permanent set.

Plasticity by historical connotation refers somehow to the characteristics of matter that have to do with the receiving and the holding of form. In practice one must distinguish between two substances which, although equally soft and yielding with equal ease to the molding pressure, yet differ in the fidelity with which they hold shape when taken out of the mold. One may retain the mold contour accurately and permanently. The other may, within some interval of time, more or less prolonged, resume to a considerable extent its original or some other shape, determined by surface tension and other forces, quite unlike that which was impressed upon it. The first is said to mold better—that is, to be more plastic than the second. The question is then—When any quantitative definition of plasticity is tentatively set up, how much should a substance be penalized in its degree of plasticity by virtue of the fact that, although it is not more stubborn in taking a new shape, it shows more variability and fickleness in holding it?

Degree of plasticity may be tested by means of sensations directly. One may judge the plasticity of a pellet of sculptor's clay or other plastic somewhat as follows: The pellet is held between the tips of the thumb and the forefinger and made to undergo some change of shape by pressure with the fingers. The force necessary to make any slight deformation is judged by the muscular effort in the fingers. The

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[1] Presented before the Division of Rubber Chemistry at the 76th Meeting of the American Chemical Society, Swampscott, Mass., September 10 to 14, 1928.

amount of deformation retained is judged by releasing the pressure at the finger-tips and observing whether or not the new shape is stable. If the deformation is given up, the actual sensation will tell that the displaced surfaces are following the retraction of the fingers. If a slight muscular effort was required to deform the pellet and if the deformation is retained by the pellet, then the pellet is said to be very plastic. The two aspects, ease of deformation and retention of form, are both felt. A substance is very plastic when it is easily deformed and when it retains the whole of the deformation given. No definition of and no mensural method for plasticity can be in contradiction with these facts.

Definition of Unit Plasticity

As a first suggestion of quantitative definition, the following is given: *A substance has unit plasticity that deforms a definite amount under some standard conditions when a force of 1 kg. per sq. cm. acts upon it for 1 second, and the whole of this deformation is permanently retained.* In this definition it is recognized that in measuring plasticity account must be taken of (1) magnitude of forces acting to give the deformation, (2) the amount of deformation retained, (3) the time during which the forces act (and time during which retention is desirable), (4) the conditions chosen as standard. The name "pla" is suggested for this unit.

Plasticity Measurement with New Plastometer

The definition of unit plasticity, with its various essential elements just enumerated, suggests more than one method of measurement. None of these need to be discussed for the present except that which concerns the new plastometer whose parts are described in detail in another paper (*9*), but whose operation, in a general way, will now be considered. For it the time factor is constant, the force is allowed to vary within certain limits, the deformation is variable within certain limits, and other conditions are kept constant.

The sample of the substances whose plasticity is to be measured is cut in the form of a small cylinder 1 cm. (0.394 inch) long and 1 cm. in diameter. This sample is placed between two jaws or fingers of the same diameters as the sample, the upper of which is movable vertically. A spring is then released which through a plunger causes the upper jaw to move downwards and impart to the sample a deformation (a change in height) depending upon its softness. The amount of this motion downwards is indicated on a dial, and is a measure of the force exerted by the spring in causing it. After this deformation has been produced, the force of the spring is suddenly removed. If the sample is very plastic according to the definition above, most of the deformation will be retained; if the sample has little plasticity and is quite elastic it will recover in short order and will retain little of this deformation. To measure the amount of this deformation that has been retained, a piston rests lightly upon the upper surface of the sample and remains in contact with it continuously, so that when the deforming force is suddenly released the amount of recovery is continuously indicated on a dial and may be read after 5 seconds.

This apparatus gives the magnitude of the force acting for a definite time, the amount of the deformation, and the portion of this deformation which is retained up to a definite time. It has thereby complied with all requirements of the quantitative definition for plasticity.

The force which the spring exerts during the deformation is related, inversely, to softness; i. e., the greater the force as indicated by the dial reading, the harder or stiffer the body. Let us call this force (in kg. per sq. cm.) F. The amount of the deformation retained, D (obtainable from dial readings), may be expressed in per cent of the initial length. Symbolically, then,

$$\text{the plasticity, } P, = C\frac{D}{F}$$

where C is a constant. In this first approximate quantitative expression there are only familiar things. F is some function of hardness determined under certain conditions, and D is some simple function of permanent set. Reflection upon the elementary sensations involved in everyday acquaintance with plasticity makes this seem rational. It is one of the simplest possible formulas suggestively defining plasticity. It may be looked upon as a general functional equation, however, and the next step is to establish just what the functions are.

Plasticity is defined, then, as the product of two functions D and s, where s is a function of softness and D a function of permanent set. The simplest case is to let the function s be equal to the softness itself, and to let D be the permanent set. Although there is good justification for the first, certain other possibilities present themselves in place of the second.

$$P = sD$$

The amount of deformation retained may be expressed in per cent of the total amount of deformation given irrespective of the magnitude of the forces involved and of the dimensions of the specimen. The word "retentivity" is suggestive here and will be tentatively adopted. The material which retains the whole of any deformation is rated 1; one that retains none is rated 0. In the first case the plasticity is entirely determined by the softness; in the second the plasticity remains zero irrespective of the softness. An illustration of the first class is the sculptor's clay; of the second, a steel spring. For the present one may rest content to suggest how some formulation may be reached for softness and retentivity in their simplest setting.

Letting h, h_1, h_2 be, respectively, the initial height, the height under compression, and the recovered height, the change in height during compression expressed in terms of the initial height is $\frac{h-h_1}{h}$. The more or less permanent change in height of the body at some definite time after the force has been removed is $\frac{h-h_2}{h}$. The ratio of these is

$$\text{Retentivity} = \frac{h-h_2}{h} \Big/ \frac{h-h_1}{h} = \frac{h-h_2}{h-h_1}$$

To arrive at some rational expression for softness is more difficult but more urgent, not only for the present inquiry into the nature of plasticity, but more fundamentally as a step toward an examination and understanding of the concept hardness. A sensual impression of softness seems to be associated directly with the yielding of material when touched or pressed. It has no regard for certain other properties; for instance, one may with propriety speak of a soft steel spring that is very elastic as well as of a soft clay that is very inelastic. There are no specific dimensional elements implied. We may compare the softness of a feather bed with that of a mat or of wax even without taking into account any dimensions, and we may compare the softness of two spring mattresses without taking into account the length of the springs. Softness sensually is an integral and gross property of a material. A "specific softness" is desired for the formulation of plasticity. Hardness, the reciprocal of softness, in the rubber industry is measured by effects of compressional forces. It is often called resistance to penetration, since the force is applied over a very small area of the sample.

As a first suggestive formulation the following may be used:

$$\text{Softness, } s, = K\ \frac{h - h_1}{h} \times \frac{1}{F}$$

where K is a constant of the apparatus and units employed. This implies that the greater the force F required for a given deformation, the harder the body; or for any given force or range of forces, the smaller the deformation, the harder the body. The range of hardness allowed is from zero to indefinitely great. When comparing samples over extended ranges of force or for some force F far removed from the conditions implied in the definition, allowance must be made for an exponent of F. This holds true also for the factor of time and perhaps for all other factors that are changed when conditions are changed. Plasticity becomes as a first approximation:

$$P = K\ \frac{h - h_1}{hF} \times \frac{h - h_2}{h - h_1} = K\ \frac{h - h_2}{Fh}$$

The above analysis is the result of an attempt to give a logical background to the proposed scheme of measurement. This certainly is preferable to a perfectly arbitrary method of procedure (*10*).

The Time Factor

The time of compression in the definition is one second. In the practical apparatus the compression goes from a minimum to a maximum in that interval. An average value is used in calculating the absolute plasticity. In the original development of the apparatus it was deemed for such small intervals of time advantageous to use a spring rather than weight, especially if one is interested in sudden release of the compressing force. The release need not be so sudden as in this apparatus. The particular intervals used should be set by the article under observation. From a broad technical view it would be desirable, however, to have all measurements of plasticity refer to some standard condition so that the values for any material that may be recorded may be comparable. Other considerations entered into the adoption of a rather short interval. One is from the viewpoint of flow. It is desirable to have any corrections which may be necessary due to small changes in the dimensions of the sample approximately proportional to the force. If the times involved are so short that equilibrium conditions of viscous flow cannot be established, or can play only a minute part, then one may expect to have simple relations. Certainly, when conditions of equilibrium for viscous flow have been established, changes in the initial dimensions of the sample may not bear any simple linear relation to the changes in the forces applied to bring about a given flow or deformation. By these statements it is not meant that plasticity may not and should not be obtained at longer lapses of time, but only that, if so made, there may be difficulty in referring back to the values obtained for the shorter intervals designated in the definitions. Either arbitrary extrapolation may be made or a great deal more of the properties of materials must be learned.

Note—This is difficult so long as the various factors involved are not known, and accurate interpolation is impossible. There is demanded a knowledge of how deformation varies with the dimensions of the body, with the force applied, and with the time and temperature; and furthermore, how the recovery from deformation depends upon these parameters.

No doubt one may at times wish to determine plasticity under extreme conditions. When plasticity is measured for purposes of control in the factory, the conditions under which measurements are made and the magnitude of factors must be so chosen that the results may readily be shown to have some simple interpretation in practice. In case of the milling and mixing of rubber and its compounds, the time intervals involved are generally very small—less than one second. For this reason also the time intervals were kept as small as practicable in the first instrument. A final point in favor of the short interval was the fact that it appears that short intervals are involved in the estimation of the property "nerve" to which experienced rubber craftsmen are wont to refer. In "nerve" not only the completeness of recovery and the magnitude of the forces exerted during recovery, but also the speed of recovery appears to enter.

Range of Usefulness of Plasticity Measurements

It may be of some interest to point out that one may be concerned with plasticity under conditions that may not pertain only to compression. Bending or torsional or extensional forces and deformations may be involved, and also changes of volume. The concepts and analysis given above may be directly applied to such cases.

The measurement of plasticity is of interest wherever the forming of articles in molds is concerned, and whenever it is desired to use deformable materials under conditions where there is not time for the equilibrium conditions of viscous flow to be set up; and even in certain cases where the interest lies rather in elasticity, such as in upholstery or felts. In cases like the latter, plasticity is an objectionable feature and its measurement may indicate how nearly this undesirable feature may have been eliminated. Industries which deal in plastic materials, as the ceramics industries; which have to do with the manufacturing of bakelite and casein articles and the like; also those dealing in the cellulose, have interest in plastometric measurements for control purposes. The measurements of plasticity may possibly be of some importance to the paper industry and certain textile industries. Plasticity should play some role in the pastry and confectionery industries. Incidentally, plasticity is a very important property of all materials that are to be masticated between teeth—that is, most foods. This suggests that the rate of change of plasticity in chewing-gums on being masticated between the teeth may be of some importance to the chewing-gum industry.

Plasticities of Some Common Materials

(Temperature, except in case of rubber, 20° C.)

MATERIAL	SOFTNESS[a]	RETENTIVITY	PLASTICITY *Milliplas*
Chewing-gum:			
Unmasticated	0.342	0.722	243
Masticated 15 times	0.284	0.843	2410
Masticated 30 times	0.256	0.814	2070
Beeswax, commercial	0.0545	0.25	13.6
Asphalt	0.0211	0.20	4.22
Cheese, Swiss	1.57	0.0424	66.4
Bread, rye	11.41	0.547	6250
Bread, rye, crust	4.40	0.0206	90.8
Beef, raw, stewing	2.54	0.211	537
Veal, raw, chop	2.27	0.289	757
Bologna, ring	4.28	0.313	1342
Steel, cast (*12*)	0.0000121	0.0278	0.00034
	0.0000129	0.0992	0.0013
Crude rubber; smoked sheet, unmasticated:			
30° C.	1.16	0.0748	8.73
100° C.	1.66	0.0305	50.7
140° C.	2.02	0.0692	139.9

[a] The unit of softness assumed in this table is that of a body of standard dimensions (1 × 1 cm.) when 1 kg. per sq. cm. compressing it for 1 second will produce a 10 per cent change in height. Some relative unit is always implied in such a table as this, even if it is not explicitly mentioned.

The critical study which led to the analysis of plasticity given in these pages was begun in connection, not with rubber, but with certain metallurgical problems involved in the working of metals, such as the drawing of tungsten and molybdenum. These concepts should have a direct bearing upon ductility and malleability and other working qualities of metals, for these properties also have to do with the molding of materials to predetermined shapes under certain practical situations in respect to the applications of the forces and the time intervals involved. Certainly, here again the factors of deformability and retentivity are concerned. In the case of wire drawing, the deformability factor may be thought of in several ways—one as follows: During the process of drawing through a die there is an orientation and alignment of the crystals. One set of the 110 planes, for example, in cubical systems such as tungsten become more nearly parallel to each other and to the direction of drawing. This alignment may be followed by use of x-ray technic and the degree of orientation estimated. The amount of orientation per unit of tractive force per unit of cross-sectional reduction is a measure of this deformability. The retentivity factor may be considered as the ratio of the difference between the initial and the final diameters of the wire and the difference between the initial diameter of the wire and the diameter of the die. The time element should be considered—either maintained constant at some arbitrary value, or the function of time determined and proper allowance made when going from one set of conditions to another involving a change of time intervals.

The temperature coefficient of plasticity of some materials such as rubber, of other thermoplastics and even of metals, and possibly of cheoplasts, has practical importance. In the rubber industry plasticity is a property of enormous importance. A large amount of data has been gathered with the use of the instrument described above bearing upon the relation of plasticity to the time and to other elements entering into the mastication of rubber, and upon the temperature coefficient of plasticity. Such data are given by Dieterich elsewhere in this issue (*4*). The thermal coefficient of plasticity may vary enormously depending both upon the pigments used and the treatment to which the rubber has been subjected during the milling and mixing operations. The plasticity rating of some common materials is indicated in a preliminary fashion in the accompanying table. The plasticity of steel is estimated from data given by Unwin (*13*). The compression in one case was 0.0157 per cent, in the other 0.118 per cent. The time factor is ignored. It is not known how to extrapolate the scale of softness for large ranges of time nor how the retentivity depends upon time factor in the deformation and in the recovery processes. Linear variation of deformation with force is implied. All these assumptions tend to make the figures higher than should be.

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Vaporization of Complex Mixtures[1,2]

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Fundamental equations applicable to the continuous and differential vaporization processes have been derived and checked by comparison with experimental data. The two different processes have been studied experimentally and theoretically and nine specific conclusions have been reached.

THE processes of vaporization and condensation are extremely important in the refining of crude oils and in the production of gasoline; yet little fundamental information is available on the two types of vaporization, continuous or "flash" and differential or "batch," as applied to complex mixtures such as gasoline. Practically the only direct experimental contribution is that by Leslie and Good (*4*), which was carried out with the purpose of comparing these two methods of vaporization as applied to petroleum. Their conclusions favored the continuous or single-flash process as used in a pipe still over the differential or batch process, largely because of the greater yield of 430° F. end-point distillate at the same final temperature.

More specific comparisons may be made if the compositions of the distillates and residues obtained from these vaporization processes are more accurately known. These compositions may be computed by use of Raoult's law or the assumption of ideal solutions, or any other similar relationship between the vapor and liquid compositions. In this paper such computations have been made and experimentally verified so as to yield nine specific comparisons between continuous and differential vaporization processes when conducted under equilibrium conditions.

Natural gasoline was chosen for this study because it is a typical commercially important complex mixture, simpler in composition than petroleum, which may be analyzed in terms of individual hydrocarbons. Furthermore, present information indicates that Raoult's law may be applied to the calculation of partial vapor pressures of such mixtures with sufficient accuracy to lead to general qualitative conclusions which may be extended to other complex mixtures not so readily susceptible to analysis or calculation.

Experimental Vaporization of Natural Gasoline

DIFFERENTIAL OR BATCH VAPORIZATION—The vaporization process with which we are most familiar consists in heating the liquid in a vessel and continually removing the vapor, as it is formed, from contact with the liquid. The vapor evolved from the liquid is always richer in the more volatile components than the residue, but both gradually become impoverished in these as the vaporization proceeds. When this vaporization process is so conducted that none of the vapor is refluxed and at such a rate that equilibrium practically obtains between the liquid and vapor phases, this process is called "equilibrium differential vaporization."

Careful differential vaporization of a sample of natural gasoline was conducted in a specially designed apparatus

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[1] Presented before the Division of Petroleum Chemistry at the 76th Meeting of the American Chemical Society, Swampscott, Mass., September 10 to 14, 1928. Received March 15, 1929.

[2] Abstracted from part of a thesis submitted by W. J. Podbielniak in partial fulfilment of the requirements for the degree of doctor of philosophy in the University of Michigan.

(Figure 1) (*7*) to prevent refluxing and at such controlled rates as to closely approximate equilibrium conditions. This process was carried out at constant pressure (757.3 mm.) in the vaporizer, by slowly raising the temperature of the oil bath surrounding the vaporizer and allowing the vapor so formed to pass out through bubble bottles, 17 and 18.

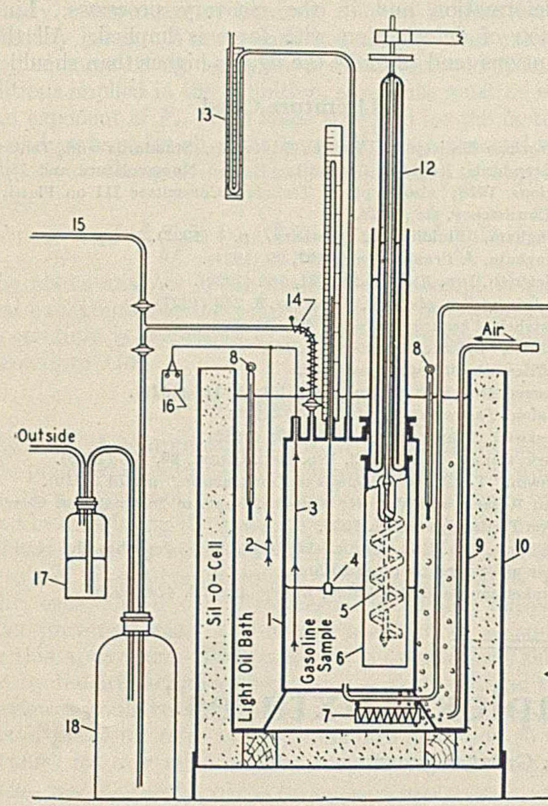

Figure 1—Differential Vaporizer

The rate of vaporization was maintained below 10 cc. a minute, so that the difference between the pressure in the vaporizer when removing vapor and when vaporization was stopped for half a minute did not exceed 1 to 2 mm. of mercury. The rate of vaporization was retarded when necessary so that the difference in temperature between the gasoline and oil bath did not exceed 0.1° C. as indicated by differential thermocouples, 2 and 3. To correct for variation in the barometric pressure the glass tube through which vapor bubbled through mercury in the bottle, 17, was periodically adjusted in the cork to keep the vaporizer pressure constant, as indicated by manometer 13.

Liquid and vapor samples were taken at regular intervals through tubes 11 and 15. The heating coil, 14, was provided to prevent condensation and reflux in the vapor line. Vaporization was continued until about half of the liquid was evaporated and seven liquid and vapor samples had been obtained and analyzed by fractional distillation (*6*).

The composition of the original liquid and vapor, and of the samples removed during the vaporization process, is given in Table I. The "corrected mol series" represents the number of mols that would have been left in the residual liquid if no liquid had been withdrawn, and was calculated from the data in the columns 2, 3, and 19.

CONTINUOUS OR FLASH VAPORIZATION—A simpler but less familiar type of vaporization is that in which the liquid is heated to such a temperature that part of it will vaporize or "flash" and the vapor so formed is maintained in contact with the residual liquid until vaporization is complete. If the vapor so formed is in equilibrium with the residual liquid, the process is known as equilibrium continuous, or single-flash, vaporization (*4*).

The apparatus used to vaporize natural gasoline by the continuous process (Figure 2) was similar to that for the flashing of petroleum described by Leslie and Good (*4*), except for modifications made necessary because of handling more volatile material. Its essentials were a feeding device, *C*, to supply material to the heating coil at a visible and controllable rate, a coil, *G*, to heat and partially vaporize the liquid previous to its admission to the equilibrium vaporizing chamber, *K*, in which the vapor produced is contacted with a liquid containing the same components, a condenser, *L*, to recover the vapor liberated in the equilibrium chamber, a residuum cooler, *N*, a constant-temperature bath, *H*, and a liquid-air trap, *Q*, for condensing the extremely volatile parts of the distillate.

The material used for continuous vaporization in this apparatus was a sample of commercial aviation fuel made by fractionating natural gasoline. This material was chosen rather than a more volatile grade of gasoline to avoid vaporization losses in the experiments. The sample was placed in the brine-cooled, 1000-cc. buret, *A*. The heating bath, *H*, was brought to the desired temperature using the heating element, *U*. Brine was circulated through the jackets of the vapor condenser, *L*, and the residuum cooler, *N*. Vent *E* was opened to air manometer *F* filled with water and stopcock *C* partially opened to allow the solution in the jacket to drop into the tube *D* and into the heating coil, *G*, the stopcock being adjusted as often as necessary to keep the rate of feed practically constant as determined by counting the number of drops per minute. The rate was always below 10 cc. per minute, which had been proved low enough to give

Table I—Data on Experimental Differential Vaporization

Gasoline Temperature[a]	Volume Residual Liquid Cor. to 0° C.	Volume Withdrawn for Liquid Samples Cor. to 0° C.	Composition of Liquid Sample, in Mol Per Cent								Composition of Vapor Sample, in Mol Per Cent						Calcd. Sp. Gr. at 0° C.	Mols per cc. (at 0° C.) of Residual Liquid	Cor. Mol Series
			Propane	Isobutane	Butane	Isopentane	Pentane	Isohexane	Hexane	Residue	Propane	Isobutane	Butane	Isopentane	Pentane	Residue			
° C.																			
21.1	10,562	140	1.43	4.66	22.81	16.10	17.20	12.70	9.50	15.60	13.92	10.75	49.31	21.06		4.96	0.669	0.008154	100
27.4	9215	78	0.59	1.96	20.30	16.62	17.90	7.60	19.28	15.74	7.68	8.95	48.60	12.90	14.06	7.81	0.672	0.008082	87.80
33.4	8140	106	0.05	0.98	15.90	14.13	19.47	18.39	14.67	16.41	2.28	8.56	46.23	16.10	16.98	9.85	0.676	0.008031	77.80
42.0	6638	0			9.70	15.52	18.33	12.42	20.40	23.63	0.00	4.93	36.15	16.08	26.76	16.08	0.687	0.0076026	61.02
45.0	6182	173			8.22	8.65	22.23	9.74	26.95	24.21	0.00	0.00	34.56	22.13	23.32	19.99	0.690	0.007496	56.03
50.7	5291	91			4.63	6.18	22.88	16.61	19.63	30.06	0.00	0.00	25.78	18.58	31.18	24.46	0.699	0.007232	47.77
52.6	4981				4.60	4.47	22.74	23.12	16.09	28.97	0.00	0.00	21.30	24.23	26.34	28.13	0.697	0.007270	46.04

[a] Total pressure was maintained at 757.3 mm. (corrected for temperature).

equilibrium between vapor and liquid in this apparatus (*4*). As soon as residue began to overflow into the receiver, *P*, the height of the indicating liquid in the manometer *F* when the vapor delivery line *L* was opened to the atmosphere was marked and vent *E* closed. The vapor delivery line was connected to the glass trap, *Q*, cooled with liquid air, and the pressure in the apparatus as read on manometer *F* maintained constant by adjusting the pressure-regulating device, *T*, as often as necessary to compensate for the increasing head of condensate in the trap, *Q*. No difficulty was found either in controlling the rate of feed or in maintaining a constant pressure in the apparatus.

After a number of preliminary runs at a vaporization temperature of 52° C. (126° F.), in which the sum of the distillate and residue checked the amount of material fed within 0.5 per cent, a final check run gave the data in Table II.

Table II—Data on Experimental Continuous Vaporization

	Grams
Material fed to apparatus	422.0
Distillate	121.0
Residue	302.5
Distillate plus residue	423.5

ANALYTICAL RESULTS

	Feed *Mol per cent*	Distillate *Mol per cent*	Residue *Mol per cent*
N-Butane	5.42	11.68	2.00
Isopentane	11.85	17.86	9.54
N-Pentane	32.10	44.56	22.77
Isohexane	13.82	12.59	11.05
N-Hexane	16.54	8.46	24.17
Residue	20.27	4.84	30.48

MATERIAL BALANCE (BASIS, 100 MOLS FEED)

	From analysis of feed *Mols*	From analysis of distillate and residue *Mols*
N-butane	5.42	5.28
Isopentane	11.85	12.36
N-pentane	32.10	30.17
Total pentanes	43.95	42.53
Isohexane	13.82	11.57
N-hexane	16.54	18.84
Total hexanes	30.36	30.41

The yield of distillate was computed to be 33.93 mol per cent of the feed and the yield of residue 66.07 mol per cent. From these percentages and from the analytical data the material balance for the individual components of the gasoline was obtained. The combined pentanes and the combined hexanes check much more closely than the individual isomers, owing largely to the difficulty in separating these isomers in fractional distillation. The discrepancies introduce relatively slight errors, as the isomers have the same molecular weight and their vapor pressures are not widely different. On the whole, the agreement is satisfactory.

Calculation of Vaporization Processes

The mathematical analysis of both the continuous or single-flash and the differential processes for any mixture is presented most simply as follows:

Let x be the composition of the liquid expressed in mol fraction. Let y be the composition of the vapor in contact with the liquid, also in mol fraction. Let w be the amount of the liquid expressed in mols.

A material balance for the components of a binary or complex mixture before and after a vaporization process, regardless of whether this vaporization is an infinitesimal step in a differential vaporization process, or a finite single flash, may be expressed as the following differential equation:

$$wx = (w + dw)(x + dx) - dw(y + dy) \qquad (1)$$

Since the only assumption involved in this equation is that of a material balance for each of the components of the mixture, it is of general application. It may be put into the integral form to define mathematically the general differential vaporization process:

$$\int_{w_1}^{w_2} \frac{dw}{w} = \int_{x_1}^{x_2} \frac{dx}{y-x}$$

of which the left-hand side is readily integrated:

$$\log_e \frac{w_2}{w_1} = \int_{x_1}^{x_2} \frac{dx}{y-x} \qquad (2)$$

When the relation between x and y is known for a differential vaporization process, the right-hand side of Equation 2 may be integrated either directly or graphically for simple cases such as binary mixtures. When the mixture is complex, Equation 2 must be expressed as a number of simultaneous differential equations representing separate material balances on the components in the mixture; the direct integration of these equations is difficult (or impossible) and extremely involved. It is possible, however, to make this integration for all cases where y can be calculated from x by modifying Equation 1 to adapt it to stepwise computation. This may be done by substituting finite values for the differentials, as follows:

$$wx = (w + \Delta w)(x + \Delta x) - \Delta w(y + \Delta y)$$

and

$$\frac{wx + \Delta w(y + \Delta y)}{w + \Delta w} = x + \Delta x \qquad (3)$$

If the differential vaporization process to be computed is regarded as a series of successive small finite vaporizations or single flashes, Equation 3 may be used to compute each step or single flash, provided Δw is given a sufficiently small value (preferably a constant small per cent of w) to make $\Delta w \Delta y$ the product of two small quantities, small enough not to affect the accuracy desired in the results. In the following computation of the experimental differential vaporization process, Raoult's law is used to calculate the composition of a vapor in equilibrium with liquid.

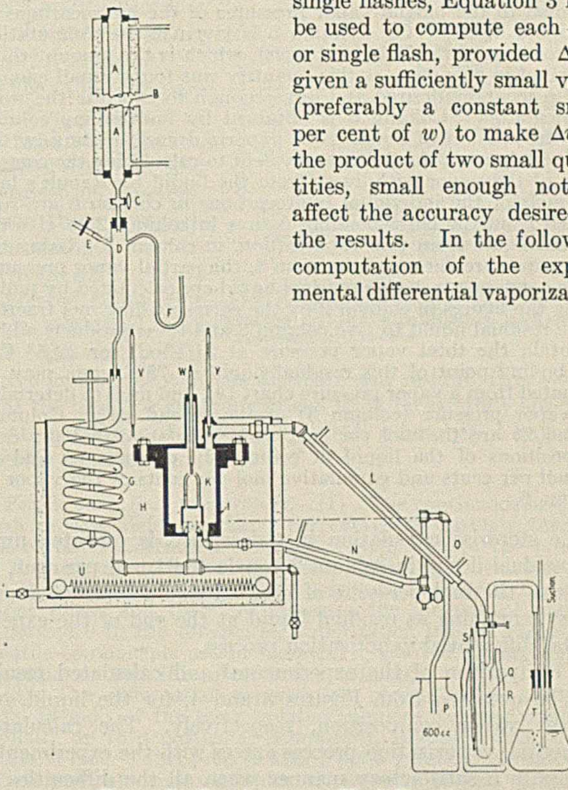

Figure 2—Continuous or Flash Vaporizer

DIFFERENTIAL PROCESS—The experimental differential vaporization process was carried out at constant pressure (757.3 mm.) with natural gasoline of the composition given

Table III—Theoretical Computation Based on Raoult's Law of Experimental Diffential Vaporization Process for Same Conditions and for Same Original Liquid Composition

(1)[a]	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(2a)	(2b)	(6a)	(6b)
					FIRST STEP						
Propane	1.214	6400	7,770	84.90 × 5% = 4.245 $\frac{4.245}{66,749}$ × (4) = (6)	0.494	0.720	57.1	1.43	1.43	11.64	11.64
Isobutane	3.956	2370	9,376		0.596	3.360	98.5	4.66	6.09	14.04	25.68
N-Butane	19.366	1635	31,663		2.014	17.352	352.1	22.81	28.90	47.46	73.14
Isopentane	13.669	597	8,160		0.519	13.150	97.4	16.10	45.00	12.23	85.37
N-Pentane	14.603	443	6,469		0.411	14.192	78.0	17.20	62.20	9.68	95.05
Isohexane	10.782	200	2,156		0.137	10.645	26.4	12.70	74.90	3.23	98.28
N-Hexane	8.066	126	1.016		0.064	8.002	12.5	9.50	84.40	1.51	99.79
Residue	13.244	10.5[b]	139		0.009	13.235	1.7	15.60	100.00	0.21	100.00
	84.900 (100.00%)		66,749		4.244	80.656	723.7	100.00		100.00	
					SECOND STEP						
Propane	0.720	6655	4,792	80.656 × 5% = 4.0328 $\frac{4.0328}{61,088}$ × (4) = (6)	0.316	0.404	35.1	0.89	0.89	7.83	7.83
Isobutane	3.360	2465	8,282		0.547	2.813	90.3	4.17	5.06	13.56	21.39
N-Butane	17.352	1710	29,672		1.959	15.393	344.0	21.51	26.57	48.55	69.94
Isopentane	13.150	629	8,271		0.546	12.604	103.7	16.30	42.87	13.53	83.47
N-Pentane	14.192	467	6,628		0.438	13.754	83.9	17.60	60.47	10.85	94.32
Isohexane	10.645	212	2,219		0.148	10.497	29.1	13.20	73.67	3.67	97.99
N-Hexane	8.002	134	1,072		0.071	7.931	13.8	9.92	83.59	1.76	99.75
Residue	13.235	11.5[b]	152		0.010	13.225	2.0	16.41	100.00	0.25	100.00
	80.656 (95.00%)		61,088		4.035	76.621	701.9	100.00		100.00	

[a] See text for significance of column numbers.

[b] In these computations the vapor pressure of the residue, left in the still after removing the hexanes, was taken as octane, based on a molecular weight determination.

in Table I as the initial liquid. The computation, based on this initial composition and pressure, consists of a number of steps each calculated exactly as shown in Table III, which gives the complete computation for the first two steps.

Column 2 gives the distribution of hydrocarbons in the total 84.900 mols used as the initial liquid charge. In column 3 are found the vapor pressures of the hydrocarbons indicated in column 1, at the boiling point (21.1° C. in first step and 22.5° C. in second step) of the liquid in column 2. Column 4 is obtained by multiplying column 2 by column 3, the products being proportional to the partial vapor pressures of the hydrocarbons in the liquid at 21.1° C. Column 5 is given to the computation of 5 per cent of the liquid (in mols), which is the amount to be vaporized in this step, as this quantity was found small enough for the accuracy desired and large enough to expedite the work of calculation. Column 6 is obtained by multiplying column 4 by the amount of liquid to be vaporized and dividing by the total of column 4, this being equivalent to calculating the composition of the vapor withdrawn from the liquid by Raoult's law. The mols of the individual hydrocarbons in column 6 are subtracted from the corresponding figures in column 2 to give the residual liquid from this vaporization, in column 7. Using the same vapor pressures as in column 3, the partial vapor pressures of the components in this residual liquid are calculated by multiplying the figures in column 2 by the corresponding mol fraction in the residual liquid to give column 8 and these products added to obtain the total vapor pressure at 21.1° C. (or 22.5° C.). The boiling point of this residual liquid at 757.3 mm. may be estimated from a vapor pressure chart (*3*), and used to determine the vapor pressure (column 3) of the second step. Columns 2*a* and 2*b* are the mol per cent and cumulative mol per cent compositions of the liquid in column 2; columns 6*a* and 6*b* are mol per cents and cumulative mol per cents of the vapor in column 6.

The stepwise calculation just described is repeated until the residual liquid in column 2 equals 46.04 mol per cent, as this was the mol per cent of original liquid (corrected mol series) remaining as residual liquid at the end of the experimental differential vaporization process.

A comparison of the experimental and calculated results may be obtained from Figures 3 and 4, for the liquid and for the vapor composition, respectively. The calculated differential vaporization process agrees with the experimental process in a satisfactory manner when all the difficulties in sampling and analysis are considered. The deviation in the line dividing the pentanes is probably due to poor separation in the fractional distillation analysis.

Although the experimental procedure was not sufficiently accurate to determine the deviation of the individual hydrocarbons from Raoult's law, the results, in Figures 3 and 4, involving about 50 per cent vaporization, indicate that Raoult's law may be used in the manner indicated to compute the results of a differential vaporization process within the limits of accuracy usually required for present engineering calculations. There is a definite tendency of the most volatile components in this sample of natural gasoline to vaporize more and for the less volatile ones to vaporize less than indicated by Raoult's law. This is clearly indicated by the fact that a vaporization step of 5 per cent used in the computation gave results closer to the experimental data than steps of 2 or 4 per cent; and by the fact that more hexane remains in the residue than is indicated by the calculations (Figure 4). These indications are in accord with the findings of Calingaert and Hitchcock (*2*) in the case of binary solutions. Even the assumption of constant vapor pressure of the residual liquid over a range of 5 per cent vaporized was not adequate to correct entirely for the positive deviation of propane in the experimental process.

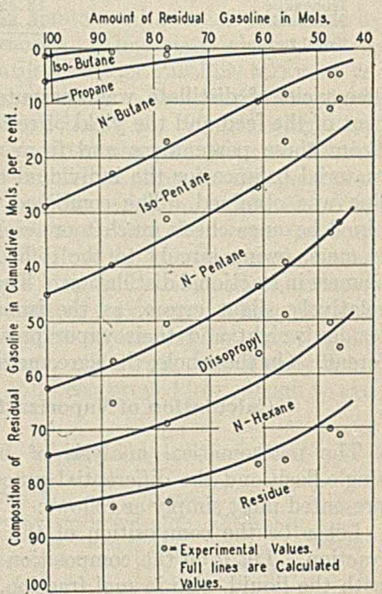

Figure 3—Computed and Experimentally Determined Composition of Residual Liquid in the Equilibrium Differential Vaporization Process

Continuous Process—Equation 3, which was used to calculate the small single flashes into which the differential vaporization process was divided for convenience in computation, may also be applied to the computation of the continuous equilibrium vaporization process. In this case the product $\Delta w\ \Delta y$ may not be neglected, and the continuous vaporization or single-flash is calculated by setting up the proper equations for the individual components on the basis of the equality of the partial vapor pressures of the individual components in the liquid and in the vapor phase as implied in the application of Raoult's law. The following nomenclature is used:

V = total mols vaporized on basis of 100 mols of feed
V (with subscript) = number of vaporized mols of component indicated by subscript
P = total flash pressure
P (with subscript) = vapor pressure of component indicated by subscript at flash temperature

Equations similar to the following, in which the left-hand side is the product of the vapor pressure of the hydrocarbon and its mol fraction in the liquid and the right-hand side is the product of the vaporization pressure by the mol per cent of the corresponding hydrocarbon in the vapor, are set up for each component.

$$P_3 \frac{(\text{mol per cent}(_3) \text{ in feed} - V_3)}{100 - V} = \frac{V_3}{V} P$$

Solving for V_3

$$V_3 \left(\frac{P}{V} + \frac{P_3}{100 - V} \right) = P_3 \frac{\text{mol per cent in feed}}{100 - V}$$

$$V_3 = \frac{\text{mol per cent in feed}}{1 + \frac{P}{P_3} \left(\frac{100 - V}{V} \right)}$$

As the vaporization pressure was 743 mm., the mol per cent of normal butane in feed, 5.42, and the total mol per cent vaporized, 33.93, these values are substituted giving a series of equations such as:

$$V_3 = \frac{5.42}{\frac{1446.8}{P_3} + 1}$$

By assuming a temperature, the vapor pressures of the individual components were fixed and the sum of the mols vaporized as computed by these equations should equal the V used in the equation. A few trials yield a check indicating that the equations have been correctly solved by trial. Assuming 52.0° C. as the temperature of vaporization, the sum of the mols vaporized equaled 34.0, which was considered sufficiently close to 33.93 as experimentally determined. Since the experimental vaporization temperature was 52.2° ± 0.2° C., the agreement is practically within the experimental error.

From the computed mols vaporized, the composition of the distillate and the composition of the residue in mol per cent may be obtained. Table IV shows the agreement of the calculated with the experimental compositions of the distillate and residue.

Table IV—Experimental and Calculated Results for Continuous Vaporization Experiment

Compound	Vapor Mol Per Cent		Residue or Bottoms Mol Per Cent	
	Exptl.	Calcd.	Exptl.	Calcd.
N-butane	11.68	11.67	2.00	2.20
Isopentane	17.86	18.47	9.54	8.44
N-pentane	44.56	44.12	22.77	25.91
Total pentanes	62.42	62.59	32.31	34.35
Isohexane	12.59	12.30	11.05	14.61
N-hexane	8.46	11.22	24.17	19.27
Total hexanes	21.05	23.52	35.22	33.88
Residue	4.84	2.22	30.48	29.58

The agreement between the calculated and experimental results is within about 2 per cent for both the residual liquid and vapor compositions when the iso- and normal pentanes and hexanes are combined, which is within the errors in sampling and analysis and is as good as the material balance in Table II.

For smaller percentages vaporized the positive deviation of the more volatile components may be more pronounced, and for more nearly complete vaporization the negative deviations of the less volatile components may be more in evidence (*2*,*5*). This applies to both differential and continuous processes, although it is more pronounced in the former owing to the cumulative effect. Since this error in the use of Raoult's law has been compensated by the stepwise calculation of the differential vaporization process, the methods outlined may be used with confidence to compare the two processes for the purpose of drawing general conclusions regarding the differential and continuous vaporization processes.

Comparison of Continuous or Single-Flash and Differential Vaporization Processes

Continuous vaporization processes were calculated (Table V) for (*a*) the same amount vaporized and (*b*) the same final temperature as the experimental differential vaporization process, using the same initial composition. Similarly, *differential vaporization* processes were calculated for (*a*) the same amount vaporized and (*b*) the same final temperature as the experimental single-flash process, using the same feed composition. The composition of the gasoline at the start of the experimental differential vaporization process is designated as Composition I, and that for the continuous vaporization experiments as Composition II. All these calculations were made according to the methods already described.

The tables compare the two processes as to final temperature, yield of distillate, and composition changes. Since these composition changes may be expressed in mols vaporized, cumulative mols vaporized, mol per cent, and cumulative mol per cent of the distillate and residue, it is evident that the basis for any comparison must be carefully specified.

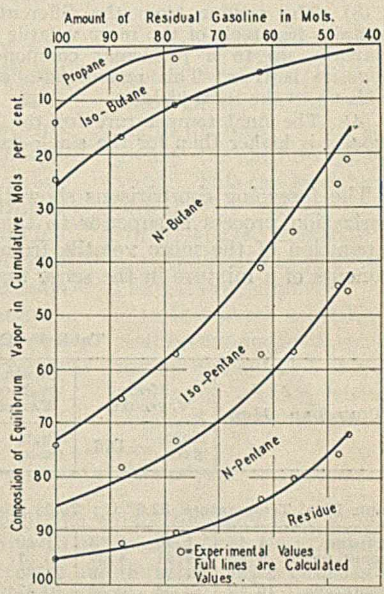

Figure 4—Computed and Experimentally Determined Composition of Vapor Evolved in the Equilibrium Differential Vaporization Process

An inspection of these tables yields a number of important specific conclusions:

For the same final temperature. (1) The continuous or single-flash process yields a greater percentage of distillate than the differential vaporization process. This is due to the presence of all the more volatile components in the vapor, which reduces the partial vapor pressure of the less volatile components in the vapor phase and therefore increases the amount of material vaporized. In the differential vaporization process these more volatile components are preferentially removed throughout the vaporization and this effect is not obtained.

(2) The differential vaporization process gives a greater yield in mols of the more volatile components compared individually up to a particular component, beyond which the opposite is true. This process also gives a greater yield in cumulative mols up to a particular component, beyond which the continuous or single-flash gives a greater yield.

(3) The total vapor from the differential vaporization process contains a greater cumulative mol per cent of the more volatile components up to 100 per cent, indicating that more of the more volatile and less of the less volatile components, proportionately, have been removed from the gasoline, or that the differential vaporization process is superior to the single flash in separation of the more volatile components from the residue.

(4) The residue from a continuous vaporization contains

more mols of the more volatile components taken individually up to a particular component, beyond which the opposite is true. The residue also contains more cumulative mols up to a particular component beyond which the opposite is true.

(5) The residue from the continuous vaporization contains a greater percentage of the most volatile and of the least volatile components than the residue from the differential vaporization process but lesser per cents of the intermediate components.

For the same mol per cent vaporized. (1) The differential vaporization process gives a greater yield in mols of the more volatile components compared individually, up to a particular component, beyond which the opposite is true. This process also yields more cumulative mols up to the total yield. The vapor from the differential vaporization process shows a greater mol percentage of the more volatile components taken individually, up to a particular component, beyond which the opposite is true; and the cumulative mol percentage of the more volatile components in the vapor is always greater than for the continuous or single-flash vapor.

(2) The residue from the differential vaporization contains less mols of the more volatile components taken individually, up to a particular component, beyond which the opposite is true. This residue also contains less cumulative mols up to the total yield.

(3) The residue from the differential vaporization process contains less mols of the more volatile components taken individually, up to a particular component, beyond which the opposite is true. This residue also contains less cumulative mols up to the total yield.

(4) The final temperature for the differential vaporization process is higher than for the single-flash.

The foregoing comparisons show that the differential vaporization process is superior to the single-flash process in separation of the more volatile from the less volatile components of a mixture in the sense that fractional distillation effects such separation. The advantage of one process over the other for the production of a particular product must be determined for each special case, as the conclusions listed above frequently involve "critical components" where the comparison reverses itself, and these components vary with the compositions of feed and product and with the conditions of the vaporizations.

Although the comparisons are obtained by computations involving Raoult's law, it is evident from the generality of the fundamental equation used that Raoult's law is merely a means to evaluate y from x for a particular case which makes it possible to accomplish the integration of this equation. All of the specific conclusions given above will hold true for a variety of relations between y and x, and may be applied to mixtures more complex than natural gasoline, for which mixtures deviations from Raoult's law may be considerable, and for a greater range of temperature and amount of vaporization. This is evident in that all conclusions refer to the various compounds as more or less volatile, and Raoult's law is simply a means of readily estimating volatility from the mol fraction or composition and is therefore simply a means to an end and not a necessary part of the above conclusions.

Applications of Methods of Computation

Although the preceding comparison of the two vaporization processes led to conclusions more or less independent of the validity of Raoult's law, the calculation of composition changes effected by either process must be based either on Raoult's law or on some other law for the relation between

Table V—Comparison of Continuous and Differential Vaporization Processes

COMPOUND	MOLS	MOLS VAPORIZED		CUMULATIVE MOLS VAPORIZED		MOL PER CENT IN VAPOR		CUMULATIVE MOL PER CENT IN VAPOR		MOLS IN RESIDUE		CUMULATIVE MOLS IN RESIDUE		MOL PER CENT IN RESIDUE		CUMULATIVE MOL PER CENT IN RESIDUE	
		Single flash	Diff.	Single flash	Diff.	Single flash	Diff.	Single flash	Diff.	Single flash	Diff.	Single flash	Diff.	Single flash	Diff.	Single flash	Diff.
Composition I																	
Same Final Temperature, 52.6° C.; 70.98 Mol Per Cent Distilled Over in Single-Flash; 53.96 Mol Per Cent Distilled Over in Differential Vaporization																	
Propane	1.43	1.40	1.43	1.40	1.43	1.97	2.65	1.97	2.65	0.03	0.00	0.03	0.00	0.11	0.00	0.11	0.00
Isobutane	4.66	4.41	4.59	5.81	6.02	6.22	8.51	8.19	11.16	0.25	0.07	0.28	0.07	0.85	0.15	0.96	0.15
N-Butane	22.81	21.18	21.53	26.99	27.55	29.84	39.90	38.03	51.06	1.63	1.28	1.91	1.35	5.61	2.78	6.56	2.93
Isopentane	16.10	13.58	10.50	40.57	38.05	19.13	19.45	57.16	70.51	2.52	5.60	4.43	6.95	8.70	12.17	15.26	15.10
N-Pentane	17.20	13.89	9.46	54.46	47.51	19.56	17.54	76.72	88.05	3.31	7.74	7.74	14.69	11.42	16.81	26.68	31.91
Isohexane	12.70	8.57	3.95	63.03	51.46	12.08	7.32	88.80	95.39	4.13	8.75	11.87	23.44	14.23	19.00	40.91	50.91
N-Hexane	9.50	5.60	2.08	68.63	53.54	7.89	3.85	96.68	99.22	3.90	7.42	15.77	30.86	13.45	16.12	54.36	67.03
Residue	15.60	2.36	0.42	70.98	53.96	3.32	0.78	100.00	100.00	13.24	15.18	29.02	46.04	45.64	32.97	100.00	100.00
	100.00	70.98	53.96			100.01	100.00			29.01	46.04				100.00		
Same Mol Per Cent Vaporized, 53.96; Flash Temperature, 42.2° C.; Final Differential Vaporization Temperature, 52.6° C.																	
Propane	1.43	1.35	1.43	1.35	1.43	2.50	2.65	2.50	2.65	0.08	0.00	0.08	0.00	0.18	0.00	0.18	0.00
Isobutane	4.66	4.05	4.59	5.40	6.02	7.50	8.51	10.00	11.16	0.61	0.07	0.69	0.07	1.33	0.15	1.51	0.15
N-Butane	22.81	18.83	21.53	24.23	27.55	34.90	39.90	44.90	51.06	3.98	1.28	4.67	1.35	8.65	2.78	10.16	2.93
Isopentane	16.10	10.50	10.50	34.73	38.05	19.46	19.45	64.36	70.51	5.60	5.60	10.27	6.95	12.16	12.17	22.32	15.10
N-Pentane	17.20	10.15	9.46	44.88	47.51	18.81	17.54	83.17	88.05	7.05	7.74	17.32	14.69	15.31	16.81	37.63	31.91
Isohexane	12.70	5.18	3.95	50.06	51.46	9.60	7.32	92.71	95.37	7.52	8.75	24.84	23.44	16.33	19.00	53.96	50.91
N-Hexane	9.50	3.08	2.08	53.14	53.54	5.71	3.85	98.48	99.22	6.42	7.42	31.26	30.86	13.94	16.12	67.90	67.03
Residue	15.60	0.82	0.42	53.96	53.96	1.52	0.78	100.00	100.00	14.78	15.18	46.04	46.04	32.10	32.97	100.00	100.00
	100.00	53.96	53.96			100.00	100.00			46.04	46.04			100.00	100.00		
Composition II																	
Same Final Temperature, 52.8° C.; 33.93 Mol Per Cent Distilled Over in Single-Flash; 30.17 Mol Per Cent Distilled Over in Differential Vaporization																	
N-Butane	5.42	3.96	4.60	3.96	4.60	11.67	15.24	11.67	15.24	1.46	0.82	1.46	0.82	2.20	1.17	2.20	1.17
Isopentane	11.85	6.27	5.99	10.23	10.59	18.47	19.85	30.14	35.09	5.58	5.86	7.04	6.68	8.44	8.39	10.64	9.56
N-Pentane	32.10	14.97	13.37	25.20	23.96	44.12	44.31	74.26	79.40	17.13	18.73	24.17	25.41	25.91	25.82	36.55	36.38
Isohexane	13.82	4.17	3.14	29.37	27.10	12.30	10.41	86.56	89.81	9.65	10.68	33.82	36.09	14.61	15.29	51.16	51.67
N-Hexane	16.54	3.81	2.65	33.18	29.75	11.22	8.78	97.78	98.59	12.73	13.89	46.55	49.98	19.27	19.89	70.43	71.56
Residue	20.27	0.75	0.41	33.93	30.17	2.22	1.36	100.00	100.00	19.52	19.86	66.07	69.83	29.58	28.44	100.00	100.00
	100.00					100.00				66.07	69.84			100.01	99.00		
Same Mol Per Cent Vaporized, 33.93; Flash Temperature, 52.8° C.; Final Differential Vaporization Temperature, 54.3° C.																	
N-Butane	5.42	3.96	4.84	3.96	4.84	11.67	14.27	11.67	14.27	1.46	0.58	1.46	0.58	2.20	0.88	2.20	0.88
Isobutane	11.85	6.27	6.71	10.23	11.55	18.47	19.78	30.14	34.05	5.58	5.14	7.04	5.72	8.44	7.78	10.64	8.66
N-Pentane	32.10	14.97	15.14	25.20	26.69	44.12	44.63	74.26	78.68	17.13	16.96	24.17	22.68	25.91	25.67	36.55	34.33
Isohexane	13.82	4.17	3.64	29.37	30.33	12.30	10.73	86.56	89.41	9.65	10.18	33.82	32.86	14.61	15.41	51.16	49.74
N-Hexane	16.54	3.81	3.10	33.18	33.43	11.22	9.14	97.78	98.55	12.73	13.44	46.55	46.30	19.27	20.34	70.43	70.08
Residue	20.27	0.75	0.49	33.93	33.93	2.22	1.44	100.00	100.00	19.52	19.78	66.07	66.07	29.58	30.07	100.00	100.00
	100.00	33.93	33.92			100.00				66.07	66.08			100.01	100.15		

the composition of a complex mixture and its vapor. When Raoult's law may be assumed to hold with sufficient accuracy, the methods of computation described in this paper are adequate for the solution of a variety of problems involving vaporization (or condensation) of such mixtures, for which substantial equilibrium between liquid and vapor may be assumed and for which the pressure-temperature conditions are known with sufficient accuracy for the purpose of the computation.

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Adjustment of Acidity of Cane-Molasses Fermentations for Maximum Alcohol Yields[1]

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In producing alcohol from cane molasses by fermentation, it is necessary to add acid to the diluted molasses in order to secure the maximum yield. It is known that the quantity of acid necessary differs with various types of molasses and even with successive shipments of a single type. A method of setting cane-molasses fermentations to the point at which maximum alcohol yield is obtained is described. The method involves the use of the potentiometer and quinhydrone electrode and has the advantage that the fermentations themselves give a check on the accuracy of the setting. Experiments show that the maximum yield is obtained when sufficient acid is added so that there is no tendency for the pH of the fermentation solution to drift toward the acid side during the fermentation.

IN THE fermentation of cane molasses for the production of alcohol a number of factors have to be taken into account in order to obtain the maximum yield from the sugar present in the fermentation solution. Such things as concentration of the solution, the temperature of fermentation, and the necessity for an adequate supply of yeast nutrients are known to have a bearing on the process. The regulation of these conditions in the actual procedure of fermentation may be fairly well carried out by combining experience with certain well-known physiological principles. This regulation is, however, a complex problem. An advance is made both in the theoretical and practical aspects of the process when it is found possible to substitute physical and chemical methods for the more empirical type of control.

One of the important ingredients in cane-molasses fermentation solutions is the acid added to bring the molasses to the condition best suited for yeast fermentation (*4*). Sulfuric acid is used ordinarily, and it is generally admitted that the amount of acid should be carefully fixed if the best alcohol yield is to be obtained. The question therefore arises as to how this acid should be regulated in different types of molasses. One method commonly used is to run small-scale fermentations with various quantities of acid (*3*). Determination of the alcohol produced in the presence of these varying amounts of acid makes it possible to pick out the proper acid dose for maximum alcohol production. This method has the disadvantage that it is tedious and requires very careful manipulation if the results are to be a reliable guide, since the absolute differences in yield between the optimum solution and the solutions not optimum are small.

It is known that the growth of microörganisms is dependent on the acidity of the solutions in which they are placed. In the case of yeast, and other organisms as well, this relation stands out when the acidity is expressed in terms of hydrogen-ion concentration rather than as titratable acid (*1*). A control method, therefore, would most logically be based on the setting of the pH of the mash to the point giving the highest alcohol yield. This can be done empirically by means of the small-scale fermentations noted above, but a more rapid method is desirable.

In this paper a method of setting cane-molasses fermentations to the point at which maximum alcohol yield is obtained will be described.

Experimental Procedure

The fermentation solutions were made from cane molasses diluted with water and with no other addition except sulfuric acid. These solutions were not sterilized, but a pure-culture yeast grown in a sterilized molasses solution was used to seed them. The seed yeast constituted 2.5 per cent of the total volume of the mash. Measurements of acidity were made with a quinhydrone electrode and a potentiometer. In carrying out the electrometric determination, 10 cc. of mash were diluted to 100 cc. with distilled water, quinhydrone added, and the reading taken. Since molasses solutions are well buffered, this 1 to 10 dilution does not materially change the pH. Alcohol was determined by distilling an aliquot and weighing the distillate in a vacuum-jacketed pycnometer. In this work it is necessary to adjust all distillate volumes at definite temperature before fermentation and at the same temperature after fermentation in order to get accurate determinations of the alcohol.

In the tables showing the results of these experiments, the acid concentration is given as cubic centimeters of 60 Bé. sulfuric per 1000 cc. of the fermentation solution. Brix readings were taken with the hydrometer and corrected to 17.5° C. The acidity was determined electrometrically at the beginning and end of the fermentation. The efficiency represents percentage of theoretical yield on the basis of the total sugar. To obtain the theoretical yield, the weight of molasses used per 100 cc. of the fermentation solution is multiplied by the sugar percentage to give grams sugar per 100 cc. The sugar percentage used is sucrose by Clerget method × 1.0528 plus the invert sugar as determined by the Munson and Walker method. This gives total as invert.

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Multiplying grams invert sugar per 100 cc. by 0.61 (number of cubic centimeters of absolute alcohol to be expected from the chemical reaction of transformation of invert sugar to alcohol, corrected for the sugar used in the formation of substances other than alcohol) gives the theoretical volume percentage of alcohol, and this divided into the alcohol actually obtained gives the efficiency figure.

First Series of Experiments

Table I gives the results of an experiment made on Porto Rican molasses.

Table I—Results with Porto Rican Molasses
(Average of duplicate experiments)

FLASK	ACID CONCN.	SP. GR. AT START	ACIDITY AT START	ACIDITY AT END	CHANGE IN ACIDITY	ALCOHOL	EFFICIENCY
	Cc.	*° Brix*	*pH*	*pH*	*pH*	%	%
1, 2	None	23.7	5.75	5.48	−0.27	8.5	83.7
3, 4	0.5	23.7	5.39	5.30	−0.09	8.6	84.8
5, 6	1.0	23.7	5.20	5.14	−0.06	8.7	85.9
7, 8	1.5	23.7	5.00	5.00	0	8.8	86.1
9, 10	2.0	23.7	4.80	4.80	0	8.8	86.1

It will be noted that if sufficient acid is added to make the pH 5.0 or lower, the fermentations do not drift toward the acid side from the beginning to the end, and that when the pH value does not drift toward the acid side, the maximum alcohol yield is obtained.

Table II shows further experiments on Cuban molasses.

Table II—Results with Cuban Molasses

FLASK	ACID CONCN.	SP. GR. AT START	ACIDITY AT START	ACIDITY AT END	CHANGE IN ACIDITY	ALCOHOL	EFFICIENCY
	Cc.	*° Brix*	*pH*	*pH*	*pH*	%	%
1	None	21.05	5.65	5.40	−0.25	7.9	89.0
2	1.3	21.05	5.05	5.00	−0.05	8.1	91.5
3	2.0	21.05	4.70	4.90	+0.20	8.1	91.5
1a	None	21.2	5.65	5.30	−0.35	7.7	87.4
2a	1.0	21.2	5.05	5.03	−0.02	7.9	90.2
3a	1.5	21.2	4.70	4.90	+0.20	7.8	88.7

These data were secured from two different lots of molasses, experiments 1, 2, and 3 having been performed on one lot and experiments 1a, 2a, and 3a, on a second lot. It will be observed that if the fermentations are set on the alkaline side of 5.0 pH they become more acid during fermentation, drifting toward 5.0 pH, and this drift is associated with a lowered yield of alcohol. Runs set on the acid side of 5.0 pH sometimes show a drift and sometimes do not. If they do change, the tendency is to move toward the alkaline side—that is, toward a point approximating 5.0 pH (*2*).

A set of experiments on another lot of Cuban molasses gave the results shown in Table III.

Table III—Results with Cuban Molasses

FLASK	ACID CONCN.	SP. GR. AT START	ACIDITY AT START	ACIDITY AT END	CHANGE IN ACIDITY	ALCOHOL	EFFICIENCY
	Cc.	*° Brix*	*pH*	*pH*	*pH*	%	%
1	None	21.2	5.60	5.40	−0.20	7.6	86.3
2	1.4	21.2	5.05	4.97	−0.08	7.9	89.8
3	2.0	21.2	4.80	4.80	0	7.9	89.8

In this series again, the drift from the alkaline side toward a pH value of 5.0 is associated with a lowered yield of alcohol in flask 1. In the case of flask 2, where the change is in the same direction but is not so large, the alcohol yield is higher. In flask 3 there is no pH change during fermentation and the yield is the same as in flask 2.

Second Series of Experiments

Several months after the experiments noted above were carried out, a second series was run using a somewhat modified technic which gave greater accuracy. Three types of molasses were used and each type was set without acid, with the optimum amount, and with twice the optimum amount. A pH of 5.0 is considered the optimum, since molasses at this acidity shows little or no tendency to become more acid during fermentation. This setting point of 5.0 pH is determined by noting the behavior of the fermentations under the particular conditions of the experiments. It should be borne in mind that under a different set of conditions this point might be at some other acidity.

The results of the experiments are given in Table IV.

Table IV—Experiments with No Acid, Optimum Acid, and Twice Optimum Acid[a]
(Specific gravity 20.0° Brix)

TYPE OF MOLASSES	ACID CONCN.	ACIDITY AT START	ACIDITY AT END	CHANGE IN ACIDITY	TOTAL ALCOHOL	EFFICIENCY
	Cc.	*pH*	*pH*	*pH*	*Cc.*	%
San Dominican, Flask 1	None	5.70	5.30	−0.40	34.56	82.46
Flask 2	1.4	4.98	5.02	+0.04	35.10	83.79
Flask 3	2.8	4.40	4.48	+0.08	35.12	83.77
Cuban, Flask 1	None	5.85	5.40	−0.45	33.87	85.46
Flask 2	1.75	5.00	5.01	+0.01	34.10	85.99
Flask 3	3.50	4.48	4.53	+0.05	34.06	85.96
Porto Rican, Flask 1	None	5.80	5.25	−0.55	36.35	84.31
Flask 2	1.16	5.00	4.83	−0.17	36.80	85.40
Flask 3	2.32	4.48	4.45	−0.03	36.92	85.76

[a] The data given in Table IV may be compared with those shown in previous tables except that the total cc. of alcohol in 500 cc. of fermentation solution is given in place of the volume per cent.

It will be noted that in every case a drift toward the acid side is associated with a lowered efficiency of fermentation. The Porto Rican molasses used needed a large dose of acid to give its best yield.

Table V gives results of experiments on two types of molasses, Cuban and Porto Rican. The experiment on Cuban molasses requires a relatively large amount of acid, and in the case of No. 3 there is a change toward the acid side even when 3 cc. of 60° Bé. sulfuric were used.

Table V—Comparison of Cuban and Porto Rican Molasses

TYPE OF MOLASSES	ACID CONCN.	ACIDITY AT START	ACIDITY AT END	CHANGE IN ACIDITY	TOTAL ALCOHOL	EFFICIENCY
	Cc.	*pH*	*pH*	*pH*	*Cc.*	%
Cuban, Flask 1	None	6.00	5.50	−0.50	34.02	85.93
Flask 2	1.5	5.28	5.02	−0.26	34.37	86.79
Flask 3	3.0	4.73	4.60	−0.13	34.40	86.73
Porto Rican, Flask 1	None	5.80	5.25	−0.55	36.58	84.82
Flask 2	1.0	5.08	4.90	−0.18	36.83	85.37
Flask 3	2.0	4.58	4.57	−0.01	37.31	86.54

Third Series of Experiments

A series of experiments, run in duplicate, was conducted as follows: (1 and 2) Cuban cane molasses solution adjusted to pH 6.25 by use of sodium hydroxide. This is well off the optimum on the alkaline side. (3 and 4) Same solution but with no addition of either acid or alkali. (5 and 6) Same solution adjusted to 5.00 pH. (7 and 8) Same solution adjusted to 4.55 pH. The results are given in Table VI.

Table VI—Experiments with Cuban Molasses of Various Acidities

EXPT.	ACIDITY AT START	ACIDITY AT FINISH	CHANGE	EFFICIENCY
	pH	*pH*	*pH*	%
1, 2	6.25	5.50	−0.75	85.74
3, 4	5.63	5.26	−0.37	85.90
5, 6	5.00	5.02	+0.02	87.18
7, 8	4.53	4.63	+0.10	86.73

Completeness of Fermentation

In connection with the results here reported, the question naturally arises as to whether the fermentations were complete in each case. This factor was followed in all the runs by weighing the flasks at intervals. Knowing the characteristics of the fermentation curve, it is thus possible to establish the fact that the fermentations are complete when the solution is distilled for determination of the percentage of alcohol.

Table VII gives the weight losses on the experiment whose results are shown in Table VI. Examination of this table shows a total weight loss of from 29 to 30 grams, which is normal for complete fermentation of the molasses under investigation. The loss in the last 12 hours was 1.5 grams or less. This very slight decrease in weight shows that the evolution of gas had practically ceased and that continuation of the experiment would result in loss of alcohol by evaporation. Data of this sort were used in each experimental run as a criterion of the completion of fermentation.

Table VII—Weight Loss from Experimental Flasks of Table VI

Flask	At 48 Hours	At 60 Hours	In Last 12 Hours	Acid Treatment
1	28.4	29.6	1.2	Received enough NaOH to bring starting pH to 6.25
2	29.3	29.8	0.5	
3	28.4	29.5	1.1	Neither alkali nor acid added, starting pH 5.63
4	28.2	29.3	1.1	
5	28.2	29.5	1.3	0.55 cc. 60° Bé. H_2SO_4 added to bring starting pH to 5.0
6	28.2	29.7	1.5	
7	28.9	30.2	1.3	1.10 cc. of 60 Bé. acid added to bring starting pH to 4.53
8	28.9	30.2	1.3	

The fermentations reported were examined under the microscope at the end of the experiments and there was no evidence that infection had played any part in determining the results.

Conclusion

The results here reported throw light on one of the factors affecting the complex process of fermentation of molasses by living yeast—namely, the acidity of the fermentation solution. They indicate that a molasses fermentation solution so adjusted that it does not become more acid during the fermentation process will give the maximum alcohol yield if other factors are kept constant. The acid concentration is measured with the potentiometer and the optimum concentration is about 5.0 pH. This is not, however, to be considered a fixed point. The real criterion for a solution optimum with respect to H ions is that there is no tendency for the solution to show a lower pH value at the end than at the beginning of the fermentation.

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X-Ray Study of the Zonal Structure of Silica Brick from the Roof of a Basic Open-Hearth Furnace[1]

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X-ray diffraction patterns by the "powder method" have been obtained for pure quartz, ganister, burned silica brick (unused), and the various zones of silica brick after the usual service in an open-hearth furnace.

The interplanar distances obtained for these materials are given, together with diffraction data on low quartz (Harrington) and high cristobalite (Wyckoff). The various lattice constants, as obtained from the literature, associated with these two forms of silica are given.

The presence of both quartz and cristobalite in burned silica brick (unused) is definitely established. Also after service in an open-hearth furnace the silica brick still retains the quartz formation, although there is a greater tendency towards the cristobalite state in the hotter zones than in the cooler zones of the brick. The probable cristobalite interplanar distances are indicated.

The x-ray diffraction method suggests itself as another procedure for the detection of the various forms of silica in silica refractories.

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IT IS of interest to those directly connected with open-hearth furnace refractories and users and manufacturers of silica brick to know just what transformations take place in a silica brick during or after service at high temperatures.

The recent researches of Greig (*3*) on the immiscibility in silicate melts establishes the temperature range at which cristobalite is in equilibrium with two liquid phases, thus determining points on the liquidus of cristobalite. This investigation has contributed a vast amount of valuable information to this field of endeavor which is also directly applicable to the changes occurring in silica brick under actual working conditions.

The usual methods for identifying the various transformations of quartz are based on density, optical methods, or the dilatometer method for volume changes at the inversions. It is known that measurements of density are unreliable, as these transformations of quartz have a low density on account of fine pores. Likewise, optical methods fail in the identification of very fine grained and porous cristobalite (*18c*), as it may appear isotropic and cannot be distinguished from amorphous silica. The dilatometer method (*20*) is the most dependable, but requires great care in the hands of a skilled operator.

In the diffraction of x-rays by fine powders and with subsequent registration on a photographic film of the different orders of reflections from the various atomic planes of a crystalline aggregate, a method is available whereby one can positively identify the constituents of ceramic and other materials, and to a much greater degree of certainty than by any optical procedure known at present. Obviously, the powder method of x-ray analysis is a very sensitive, convenient, and modern analytical procedure and one which is daily finding a wider application in the endeavor to establish with greater accuracy the real nature and constitution of matter.

There have been various applications of x-ray methods in the field of ceramics and unique data yielding entirely new information or settling doubtful and controversial interpretations of other types of data have recently been published (*1, 4, 5, 8* to *16, 19*). This investigation was undertaken to determine just what x-ray analysis would reveal in studies of burned silica brick (unused) and the zonal structure of

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[1] Received February 18, 1929.

silica brick after the usual service in the roof of an open-hearth furnace.

Diffraction of X-Rays

The so-called "powder method of crystal analysis" (*2*) has been utilized in this work. For the benefit of those not so familiar with the diffraction of x-rays by fine powders, it will not be amiss to state that the diffraction of x-rays is dependent upon the principle that in very finely powdered crystalline substances the very small crystals have a random orientation, thus making all possible angles with the incident primary beam of x-rays, so that all orders of reflections from all possible atomic planes will occur. Then when a narrow beam of monochromatic x-rays passes through a fine powder specimen (200 mesh), there will be a strong reflection from one set of parallel planes of the particles turned at the correct angle to the incident primary beam. Other particles turned at another angle will cause reflection from another set of parallel planes. If the beam of x-rays passing through a fine powder is allowed to fall on a narrow photographic film bent around the arc of a quadrant cassette, the entire diffraction pattern from the various sets of atomic planes in the powder specimen may be photographed simultaneously. The resulting photograph will have the appearance of a line spectrum, each line corresponding to one set of planes from which the interplanar distances may be measured by a special slide rule on which is mounted a scale graduated in Ångström units (1 Å. = 1 × 10^{-8} cm.).

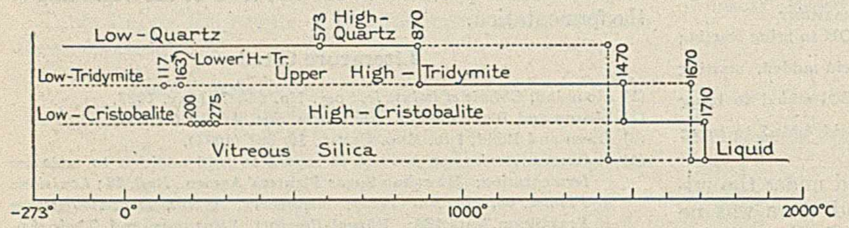

Figure 1—Graphic Representation of the Relations between the Forms of Silica (Solid Lines Represent Stable States; Dotted Lines, Unstable States)

Apparatus

In this study the well-known multiple diffraction apparatus was used. This is equipped with a Coolidge type x-ray tube having a water-cooled molybdenum target. By means of a zirconium dioxide filter all radiation was absorbed except the MoKα doublet. The standard reference material, sodium chloride, and the material under observation were both placed in Pyrex glass tubes (0.6 mm. inside diameter) separated by a tiny plug of cotton. The diffraction patterns of the two substances were thus obtained simultaneously on the same film. The x-ray tube was operated at 20 milliamperes and an impressed electromotive force of 30,000 volts.

Silica Modifications

It is known that silica can exist in eight fairly well established modifications. The temperature ranges of stability as given by Sosman (*18a*) are shown by the graphical representation of Figure 1.

Quartz to Tridymite. The direct inversion of quartz to tridymite by heat alone has never been observed. Direct heating of quartz nearly always causes it to change to cristobalite. The conversion to tridymite, however, occurs most readily when in contact with a liquid melt or flux in the temperature range 870° to 1470° C. It is said that the quartz probably dissolves in the molten flux and then crystallizes out as tridymite. This seems to be the state of affairs of tridymite as found in silica brick.

Quartz to Cristobalite. There is no true inversion temperature of quartz to cristobalite at atmospheric pressure. According to Sosman (*18b*), a metastable equilibrium is possible, thus a metastable inversion temperature at which quartz and cristobalite would coexist in equilibrium would be possible. This temperature lies below 1250° C. Above 1470° C. quartz inverts to cristobalite. The range of its stability, as seen from Figure 1, extends to its melting point, 1713° ± 5° C. The rate of transformation of quartz into cristobalite is dependent upon the state of subdivision and the temperature.

Tridymite to Cristobalite. The temperature of equilibrium between tridymite and cristobalite is 1470° ± 10° C.

At the inversion points the rate of transformation of these polymorphic forms of silica is not relatively rapid; however, above these temperatures the rate increases fairly rapidly. In the presence of liquid melts, such as molten silicates formed from low-fluxing impurities and above 1100° C., these inversions of silica are very appreciably hastened.

Production of Silica Brick

In the manufacture of silica brick the natural ganister (nearly pure quartzite) is mixed with about 1.5 to 2.5 per cent of lime, then heated slowly in kilns and finally burned at cones 18 to 20 (1490° to 1530° C.). This temperature is maintained for about 48 hours, after which the bricks are allowed to cool slowly. The composition of the burned bricks is about 96 per cent silica, 2.0 per cent lime, with small amounts of alumina, iron oxides, magnesia, and alkalies. These newly burned bricks have an open pore space of about 25 per cent by volume.

During the burning process the silica undergoes the various transformations as described above, ultimately forming a structure which is largely cristobalite (about 70 per cent) with a small percentage of tridymite and unaltered quartz (about 25 per cent).

The effect of low-fluxing oxides, especially calcium oxide and iron oxides, on the transformation of silica is to hasten the transformation to the stable high-temperature forms, tridymite and cristobalite, respectively (*7, 21*).

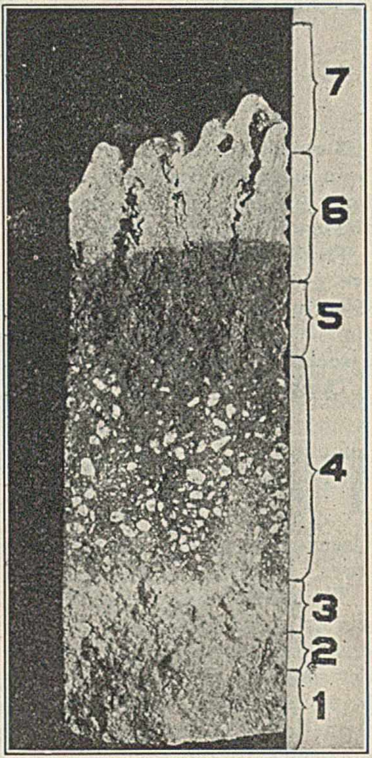

Figure 2—Fractured Silica Brick after Service in Open-Hearth Furnace

Effects on Silica Brick in the Open-Hearth Furnace

During the operation of an open-hearth furnace the inner ends of the silica brick reach a prevailing temperature in the neighborhood of 1600° C. It is to be expected that any unaltered quartz, in the hotter portions of the brick, will un-

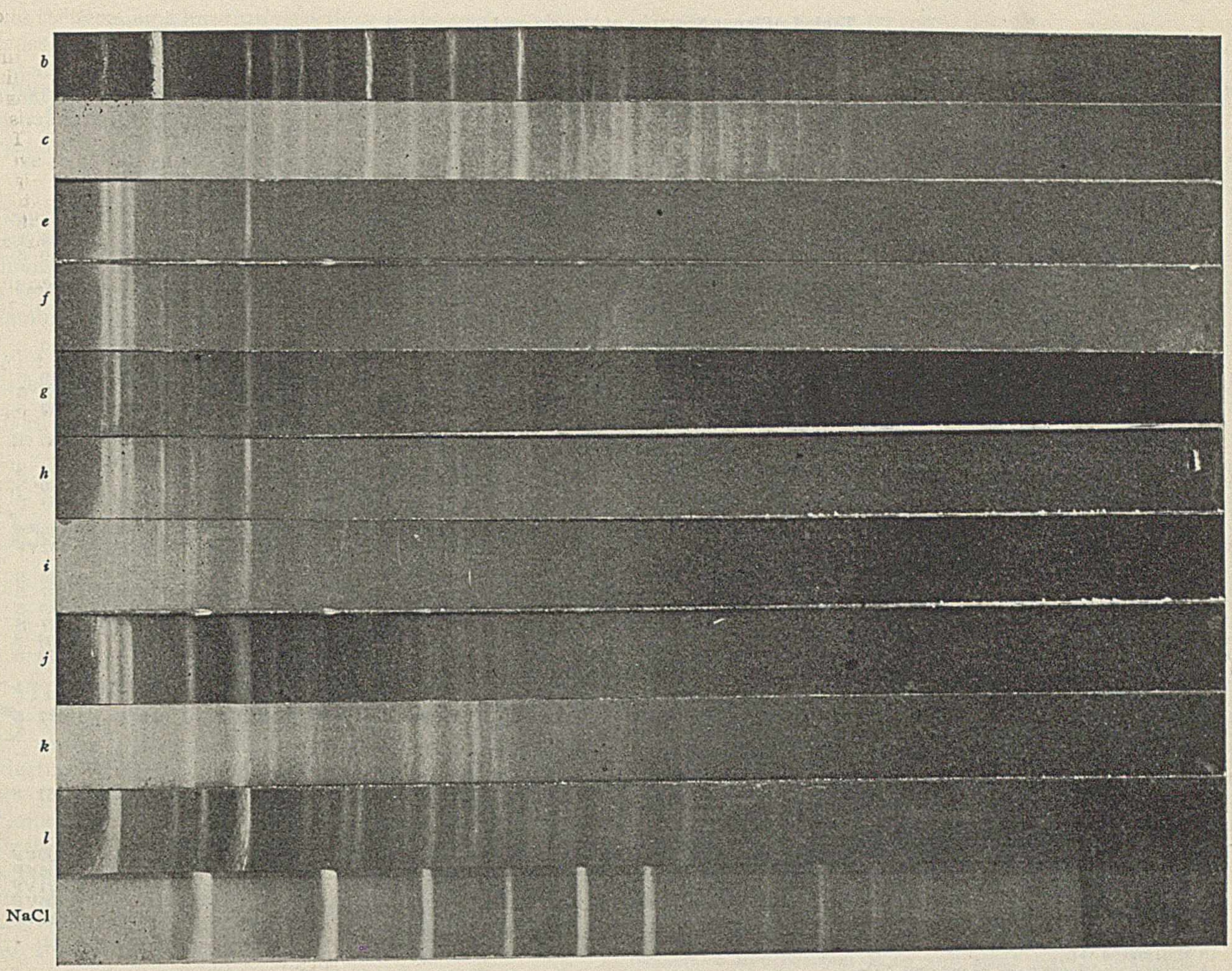

Figure 3—Diffraction Patterns of Zonal Structure of Silica Brick

dergo transformation producing the stable forms for the various temperature ranges. Also, the low-fluxing impurities originally in the brick and the silica will form a liquid melt with a gradual filling in of the open pore spaces yielding a rather homogeneous structure, with the added tendency to hasten the inversion of silica to cristobalite. Eventually an equilibrium between cristobalite and the liquid phase will be established.

Another factor for consideration is the effect produced by the presence of fine particles of low-fluxing oxides, particularly the iron oxides, which are continually being volatilized from the molten bath of metal and slag and mechanically carried upward by the furnace gases. This fume constantly bombards the roof of the furnace combining with the silica of the brick to form a liquid phase, gradually reaching a state of equilibrium with the solid cristobalite, resulting in a further filling in of the open pore spaces of the brick. Thus the roof surface of the furnace becomes coated with a film of liquid. The stage is ultimately reached when, on account of this constant fluxing action, the volume of liquid on the roof surface becomes so great that it drops from the ceiling or flows down the walls of the furnace. This gradual corrosive action is, of course, inevitable under the existing conditions.

X-Ray Examination of Zonal Structure of Silica Brick after Service in an Open-Hearth Furnace

As can be seen from Figure 2, showing a fractured silica brick after service, there is a distinct zonal structure. In this investigation the brick was divided into seven zones, according to the differences in the outward appearance of the structure of the fracture. These zones are indicated in Figure 2. Representative portions of each zone were crushed and finally ground in an agate mortar. The material which passed through a 200-mesh bolting cloth was placed in the specimen tube along with the standard reference material, sodium chloride. The sample tube was then mounted in the holder of a quadrant cassette. A beam of x-rays defined by a slit was then passed through the powder specimens. A zirconium dioxide filter placed in front of the films absorbed all radiation except the MoKα doublet. These specimens were exposed for 72 hours. Figure 3 shows typical x-ray diffraction patterns of the zonal structure.

For comparative purposes the structure of an unused burned silica brick was also examined in the manner described above. Also the diffraction patterns are shown for pure silica and for the ganister.

The planar spacings of the crystals represented by the lines on the powder photograph (Figure 3) were obtained directly by use of a slide rule on which is mounted a scale graduated in Ängströms. The zero position is determined from the known planar spacings of sodium chloride. Table I gives the complete data for all the specimens examined, together with the interplanar spacings of high cristobalite at 290° C. according to Wyckoff (*22*). The planar spacings for low quartz as given by Harrington (*6*) have been included for reference.

Table I—Planar Spacings of Quartz and Silica Brick

Line	Low Quartz[a] (a)	Purified Quartz[b] (b)	Ganister[c] (c)	High Cristobalite[d] (d)	Interior of (unused) Burned Silica Brick (e)	Zone I (f)	Zone II (g)	Zone III (h)	Zone IV (i)	Zone V (j)	Zone VI (k)	Zone VII (l)
1		4.29 S	4.21 F		— 4.30 SS	4.30 SS	4.31 SS	4.30 SS	4.25 S	4.30 SS	4.27 SS	
				4.142								
2					— 4.40 SS	4.05 SS	4.05 SS	4.02 SS	4.00 SS	4.07 SS	4.08 SS	3.96 SS
3					— 3.81 SS	3.81 SS	3.80 SS	3.81 SS	3.81 SS	3.79 SS	3.82 SS	
4	3.32	3.37 SS	3.32 SS		3.31 VF	3.35 F	3.32 F	3.32 S	3.32 S	3.35 VF	3.39 VF	
5					— 3.22 VF	3.22 F	3.22 VF	3.20 VF		3.20 VF	3.21 VF	
6					— 3.10 F	3.12 F	3.12 VF	3.12 VF				3.12 S
7					— 2.965 F	2.978 F	2.964 F	2.97 F	2.965 S	2.975 S	2.970 S	2.965 F
8					— 2.826 F	2.816 F	2.826 F	2.818 F	2.820VF	2.820VF	2.800VF	2.820 S
				2.527						2.719VF	2.730VF	
9	2.45	2.47 S	2.45 S		2.475 S	2.476 S	2.475 S	2.480 S	2.466 S	2.500SS	2.512 S	2.495 S
10					— 2.368VF	2.370VF	2.368VF	2.370VF	2.318VF	2.316VF	2.312 S	
11	2.28	2.285 S	2.275 F		2.303VF	2.30 F	2.287VF	2.285 F				
12		2.245 F				2.233VF	2.225VF	2.210VF				
13	2.12	2.135 S	2.124 F		2.103VF	2.097VF	2.126 F	2.100 F	2.124VF	2.120 F		2.110 S
				2.072						2.064 F	2.085 S	
14	1.975	1.991 S	1.982 F		2.016VF	2.025VF	2.030VF	2.025VF	2.025VF	2.030 F	2.030 F	2.020 S
15					— 1.930VF	1.947 F	1.951 F	1.945VF		1.952VF		1.920 S
16	1.815	1.828 S	1.813 S		1.837VF	1.841 F	1.841 F	1.842 F	1.841 F	1.836 F	1.837VF	1.862 S
				1.781								
17	1.665	1.671 S	1.664 F		1.682VF	1.690 F	1.690 F	1.695 F	1.689VF	1.690 S	1.690 S	1.685 F
				1.639								
18					— 1.603 F	1.604 F	1.603 F	1.608 F	1.606 F	1.608 S	1.614 S	1.609 S
19	1.540	1.548 S	1.540 S		1.528 F	1.532 F	1.533 F	1.534 F	1.532 F	1.526 S	1.526 S	1.530 S
20					— 1.491VF	1.492VF	1.488VF	1.500VF	1.483VF	1.478 S	1.483 S	1.489 S
21	1.452	1.457VF	1.450VF	1.456								
22	1.415				— 1.430VF	1.432 F	1.431 F	1.433 F	1.439 F	1.432 F	1.440 S	1.426 S
23					— 1.398VF	1.400 F	1.402 F	1.403 F	1.400 F	1.402 F	1.409 F	1.392VF
24	1.378	1.379 S	1.372 S	1.374	1.372	1.370 F	1.370 F	1.372 F	1.371 F			
25					— 1.333VF	1.340VF		1.340VF	1.339VF	1.341VF		1.345 S
26	1.286	1.290 F	1.283 F		1.290VF	1.290VF	1.290VF	1.293 F	1.290 F	1.290VF	1.294 F	1.297 S
27	1.255	1.262 F	1.252 F	1.262								1.280 S
28	1.228	1.236 F	1.228VF		1.235VF	1.237VF	1.238VF	1.239 F	1.239VF	1.234VF	1.239 F	1.227 S
29	1.199	1.203 S	1.198 F	1.204								1.203 S
30	1.183	1.188 S	1.179 F		1.178VF	1.190VF	1.190VF	1.190 F	1.189 F	1.191 F	1.197 F	1.178 S
31	1.154	1.159VF	1.153VF		1.153VF	1.152VF	1.155VF	1.154 F	1.152 F	1.148 F	1.150 S	
32		1.122VF		1.126							1.122VF	
33		1.113VF										
34					— 1.095VF	1.098VF	1.095VF	1.100VF	1.102VF	1.091 F	1.093 F	1.097 S
35	1.081	1.087 F	1.081 F	1.086								
36		1.050 F	1.048VF			1.043VF		1.050VF				
37	1.044	1.042 F	1.035VF	1.032								
38	1.016	1.019 F	1.014VF									
39	0.991	0.987 F	0.990VF	0.994				0.992VF		0.993VF		0.981 F
40		0.959VF	0.959VF	0.950							0.972VF	
41				0.925						0.968VF		
42	0.916	0.914 F	0.913 F								0.939VF	
												0.909VF
											0.857VF	0.856VF
												0.821VF
												0.805VF
												0.782VF

SS = very strong; S = strong; F = faint; VF = very faint; — = probable cristobalite lines.

[a] Harrington (*6*).

[b] Baker and Adamson, 99.98 per cent SiO_2.

[c] General Refractories Company, through courtesy of R. P. Heuer.

[d] Wyckoff (*22*).

The zones of a silica brick from the roof of an open-hearth furnace are as follows:

Zone I—Outer edge, cool zone, approximately 1 inch (25 mm.) thick.
Zone II—Region adjacent to zone I, $^1/_2$ inch (13 mm.).
Zone III—Next to zone II, $^5/_8$ inch (16 mm.).
Zone IV—Region next to zone III, 3 inches (76 mm.).
Zone V—Next to zone IV, 1 inch (25 mm.).
Zone VI—Region next to zone V, $1^3/_4$ inches (44 mm.).
Zone VII—Slag zone, $1^3/_4$ inches (44 mm.).

LOW-QUARTZ LATTICE—It is known with a fair degree of certainty that low quartz has a hexagonal structure (Bragg, Wyckoff, and McKeehan) and that there are three atom triplets in each hexagonal cell unit. The lattice constant as reported by Harrington (*6*) has been found to be $a_0 = 4.903$ Å. and the height of prism $c_0 = 5.393$ Å., corresponding to an axial ratio of $c_0/a_0 = 1.100$.

The measurements of Siegbahn and Dolejsek (*17*) of the lattice of low quartz give the interplanar distance, d, at 18° C. as 4.246 Å. for planes parallel to a face of the hexagonal prism. The lattice constant $a_0 = 4.9035$ Å.

HIGH-CRISTOBALITE LATTICE—The research of Wyckoff (*22*) on high cristobalite assigns to this form of silica the structure of a unit cube, with length of edge $a_0 = 7.12 \pm 0.001$ Å. (the smallest dimension which repeats itself periodically in the structure) at 290° C. From density relations the value for a_0 has been checked and the number (m) of molecules of the formula SiO_2 contained within a unit cube with $a_0 = 7.12$ Å. has been calculated to be 8.03. In other words, the cubic unit cell of high cristobalite which accounts for all of the powder reflections contains 8 molecules of SiO_2.

LOW CRISTOBALITE—The symmetry of room-temperature cristobalite is not known.

Conclusions

An unused burned silica brick is composed principally of both unaltered quartz and cristobalite. During the usual period of actual service in an open-hearth furnace, the silica must undergo the various transformations characteristic of this material at different temperatures of inversion. Then after a long period under the influence of the high temperature of the furnace and in the presence of liquid phase, one would expect that practically all of the quartz would be transformed into cristobalite, especially in the hot zones of the brick. However, x-ray diffraction patterns indicate very strongly that relatively few quartz lines disappear in the portions taken from the hot zones (V and VI). Close scrutiny of the films reveals that the relative intensity of the cristobalite lines is greater in the hot zones than in the cooler zones, indicating a strong tendency towards the cristobalite formation in this region. The differences in the relative intensity of the quartz lines in the hot zones and cooler zones are practically indiscernible.

Since an unused burned silica brick is one of the best sources of cristobalite and also contains unaltered quartz, and having obtained the interplanar distances for both quartz and the cristobalite quartz brick from the x-ray diffraction patterns, it seems very likely that by eliminating the quartz lines the remaining lines are reflections of the various atomic planes of low cristobalite.

It should be noted that the lines of high cristobalite as obtained by Wyckoff are fewer in number than the probable low-cristobalite lines, indicating a marked difference in the crystal structure of low cristobalite.

Acknowledgment

Sincere thanks are hereby expressed to C. W. Parmelee, head of the Department of Ceramics at the University of Illinois, for his interest in this investigation which has led to several coöperative researches, and also for his critical examination and approval of the manuscript.

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Oxidation Mechanisms of the Paraffin Hydrocarbons[1]

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STUDY of the oxidation mechanisms of the paraffin hydrocarbons is becoming increasingly important owing to their bearing on two major problems—the industrial utilization of these hydrocarbons by converting them into oxygenated products, and the study and prevention of knocking in internal-combustion motors. The voluminous literature on the oxidation of the paraffins records many conflicting theories as to the course taken by this process. In this communication are presented the mechanisms which have been proposed, with the facts supporting and conflicting with them, thus summarizing our knowledge in this field.

Early Theories

An early theory of oxidation of the gaseous paraffins presumed the preferential combustion of hydrogen, a theory, to quote Bone and Drugman (*9*), "which would never have gained currency had not chemists ignored Dalton's classical experiments on the combustion of methane and ethylene." In 1808 Dalton (*25*) exploded marsh gas with an equal volume of oxygen, and obtained the same volumes of steam, carbon monoxide, and hydrogen.

Somewhat later Kersten (*42*) supposed that the carbon burned preferentially to hydrogen, either by direct oxidation of the hydrocarbon with the formation of carbon monoxide and hydrogen or by oxidation of the carbon after dissociation of the molecule. This theory was supported on thermochemical considerations by Smithells and Ingle (*54*) and was revived by Misteli (*50*). It was thoroughly disproved, however, by Bone and Drugman (*9*). They showed that in the explosion of the paraffins "there is always a considerable separation of carbon and a large formation of steam," which would indicate that there was certainly no preferential combustion of carbon. Further work convinced them that the slow and rapid combustion of these hydrocarbons followed much the same course. They stated (*9*):

> In arguing that there is no essential difference between the mechanism of combustion below and above the ignition point, we do not, of course, infer that the phenomena observed at low temperature, in slow combustion, are exactly reproduced in flames. We mean rather that the result of the initial encounter between the molecules of hydrocarbon and oxygen is probably much the same in both cases, namely, the formation of an "oxygenated" molecule.

Their experiments of the oxidation of gaseous hydrocarbons in mixtures with hydrogen and oxygen cast doubt on dissociation as a preliminary to oxidation.

> It does not appear that except in a very limited supply of oxygen, a hydrocarbon is to any great extent decomposed in the flame, much less than it is resolved into its elements before its actual combustion begins.

Additional support of this point of view is given by the work of Bone and Wheeler (*12*), who circulated methane and oxygen at 450° to 500° C. and were unable to detect either hydrogen or carbon at any stage in the oxidation.

Hydroxylation Theory

The mechanism of oxidation of the paraffin hydrocarbons which has had widest acceptance is the hydroxylation theory of Bone (*8, 9, 11, 12, 13, 14*). This postulates the successive formation of hydroxyl compounds, each of which may gain additional hydroxyl groups, or may lose water and break down in one or more ways. According to this theory, methane would form, first methanol, and then methylene glycol. This would pass to formaldehyde, which in turn would yield formic acid, or decompose into carbon monoxide and hydrogen. Bone and his co-workers believed that their results gave strong support to this theory. Convinced that the only alternative to hydroxylation was the preferential burning of carbon, they considered that the evidence already cited against preferential oxidation supported their thought. They were able to show that most of the substances called for by their theory were found as products of oxidation of the gaseous paraffin hydrocarbons. By slow oxidation, ethane, for example, yielded water, formaldehyde, acetaldehyde, ethylene, acetylene, hydrogen, and oxides of carbon. On explosion this hydrocarbon yielded much the same products. For all these it was possible to account by the hydroxylation theory, while they considered the early formation of water,

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[1] Presented under the title "The Mechanism of Paraffin Hydrocarbon Oxidation" as a part of the Combustion Symposium before the Divisions of Gas and Fuel Chemistry and Petroleum Chemistry at the 77th Meeting of the American Chemical Society, Swampscott, Mass., September 10 to 14, 1928. Received February 2, 1929.

unsaturated hydrocarbons, and aldehydes as further evidence for their mechanism. "We think the facts are, as a whole, best interpreted on the supposition that hydroxylated molecules are formed in flames, as they undoubtedly are at lower temperatures." (*9*)

Criticism of the Hydroxylation Theory

It should be noted, however, that among the oxidation products of ethane listed there are lacking those which are essential to the proof of the hydroxylation theory—namely, the mono- and di-hydroxy derivatives of the hydrocarbon. Nor is this an isolated case. Usually the earliest formed substances that can be identified among the oxidation products of a gaseous paraffin hydrocarbon are water and an aldehyde. The alcohol, which is presumed to be the primary oxidation product, is reported in only a few of the researches on oxidation of the gaseous paraffins which have been published. In 1923 Wheeler and Blair (*60*) stated: "Methyl alcohol has not, up to the present, been detected among the products of slow oxidation of methane." It "is the only intermediate which has not been detected. Bone has deduced its formation from a study of the detonation of methane under various conditions." Bone and Drugman (*9*) reported water and formaldehyde as among the first products of the oxidation of methane below its ignition point. They found no methanol. Wheeler and Blair (*60*) write: "An excess of oxygen inhibits the oxidation of methane little, if any, more than an excess of methane, so that if the law of mass action applies the equimolecular reaction to formaldehyde would seem to be occurring." Bone and Drugman (*9*) are not in harmony with this view, stating as evidence for the formation of mono-hydroxy derivatives of hydrocarbons that, "whereas an excess of oxygen over and above an equimolecular ratio greatly retards the combustion, a corresponding excess of the hydrocarbon had but little, if any, retarding effect."

According to Layng and Soukup (*43*):

> A thermodynamic analysis of the partial oxidation of methane and ethane on the basis of Nernst's thermodynamic theorem, as well as by integration of the available specific heat data, indicates that formaldehyde is the most probable product of the reaction if the oxidation process is considered from a kinetic as well as a static aspect. This analysis, however, does not take into consideration the effect of catalysts in altering the reaction velocities of equilibria involved in partial oxidation, so that the isolation of alcohols by direct oxidation of hydrocarbons is not impossible, though apparently difficult.

The gaseous paraffins above methane form aldehydes on oxidation, but rarely alcohols. Bone and Drugman (*9*) write: "The slow combustion of ethane involves the early formation of acetaldehyde and steam." Propyl and butyl alcohols have not been obtained from propane and butane, respectively, although the presence of aldehydic substances among the oxidation products of these hydrocarbons is readily shown (*9*).

On the other hand, in a few oxidation processes the primary alcohols have appeared. Methanol, with formaldehyde, is produced commercially by the oxidation of natural gas by a process in regard to which little has been published (*40*). In oxidation of methane under the action of the silent discharge it has been possible to establish the formation of some methanol (*31*). Layng and Soukup (*43*) obtained methanol by oxidizing methane in the presence of oxides of nitrogen. Similarly, Bone and Drugman (*10*) obtained ethyl alcohol by the interaction of ethane and ozone at 100° C.

But even in the cases in which alcohols can be identified, the hydroxyl compounds do not appear to be the primary products of the reaction. Thus Layng and Soukup isolated eight times as much formaldehyde as methanol. In a patent issued to the Traun Research Laboratory (*57*), in which it is stated that on heating methane with carbon dioxide as a source of oxygen both methanol and formaldehyde are formed; rapid passage of the gas is reported to favor the formation of formaldehyde, slow passage that of methanol. If this statement is accepted, the formation of methanol, rather than being the primary reaction, appears to be a secondary process.

The non-appearance of the primary alcohol in many cases of oxidation has been thought to be due to its rapid decomposition or further oxidation. Of the oxidation of ethane, Bone and Stockings (*11*) write:

> The first stage we have been able to distinguish involves the rapid formation of acetaldehyde and steam. There is no direct evidence of the primary formation of any ethyl alcohol. But as we find that ethyl alcohol is, under similar conditions, oxidized far more rapidly than ethane itself, we cannot attach any significance to its non-occurrence.

Work on the higher paraffins, however, has cast considerable doubt on Bone's assertion that the lower alcohols oxidize so rapidly that they could not be detected if formed. Layng and Youker (*44*) observed that *n*-heptyl alcohol was very difficult to oxidize, much more difficult than *n*-heptane or *n*-heptyl aldehyde. Callendar (*17*) found that the higher primary alcohols had higher temperatures of initial combustion than the corresponding hydrocarbons and that "methyl, ethyl, butyl, and amyl alcohols are much less readily oxidized by air than hexane and similar hydrocarbons."

Moreover, as has been shown, in some cases of oxidation, the presence of the alcohol in the products can be established. If the alcohol is so much more easily oxidized than the hydrocarbon, it would not be expected to appear in any oxidation process. One is led to believe that in the majority of oxidations, in which aldehydes but no trace of alcohol can be detected, the hydroxyl compound is not formed.

By oxidizing methane with nitrogen peroxide, Frolich, Harrington, and Watt (*33*) obtained formaldehyde in amount equivalent to 20 per cent of the methane decomposed, but no methanol. They attributed this primarily, not to the further oxidation of this substance, but to its thermal decomposition, pointing out that above 300° C. in its equilibrium with carbon monoxide and hydrogen, the alcohol is present in very small amounts. They believed that the alcohol formed but was immediately decomposed. This does not seem probable. Working at temperatures fully as high as did these investigators, Layng and Soukup (*43*) were able to obtain appreciable amounts of methanol. Moreover, if in the oxidation process methanol forms and decomposes into carbon monoxide and hydrogen, it is difficult to account for the large yields of formaldehyde which have been reported, sometimes amounting to 70 per cent of the methane consumed (*58*). It seems unlikely that this formaldehyde would come from carbon monoxide and hydrogen.

Another assumption in the theory of Bone that is open to question is the oxidation of alcohols by way of the dihydroxyl compounds. Work of Wieland (*61*) has indicated that in some cases the formation of the aldehyde from the primary alcohol takes place by direct dehydrogenation rather than by further hydroxylation. The existence of compounds in which two hydroxyl groups are attached to the same carbon atom has been demonstrated in but a very few cases. Evidence is lacking of the formation of the simple alkylidene glycols.

Callendar (*17*) has criticized the hydroxylation theory because he found no hydroxyl compounds among his oxidation products and because their formation would require that reaction be preceded by disruption of the oxygen molecule. To him this appeared very unlikely, owing to the low temperature at which some of his oxidations were carried out. Moreover, he stated that such division of oxygen molecules could hardly fail to be accompanied by ionization, of which he found no evidence. Bennett and Mardles (*6*) have raised the same objection, stating that the scission of oxygen molecules into atoms would probably bring about liberation of electrons, whereas in no case did they detect ionization before the initial oxidation.

Later Theories

Using the work of Bone as substantiation, Armstrong (*2*) claimed the slow oxidation of methane to be a series of hydroxylations in which water took part and the oxygen molecules reacted as units, so that dihydroxy derivatives of the hydrocarbons and hydrogen peroxide were formed. The formation of dihydroxy compounds or hydrogen peroxide, however, was not proved. Bone and Drugman (*9*) strongly opposed this view, believing that the oxygen was conveyed to the hydrocarbon directly and not through the intervention of water. As to the necessity of the oxygen reacting as molecules, they answered that, at least in flames, the oxygen was probably not present in ordinary molecular form. They also pointed out the difficulty, from a kinetic standpoint, of assuming as a preliminary to reaction the simultaneous conjugation of hydrocarbon, water, and oxygen. From their study of the relative rates of oxidation at low temperatures of various mixtures of ethane and oxygen, ethylene and oxygen, acetylene and oxygen, they obtained evidence which they considered conclusive, that a monohydroxy, and not, as suggested by Armstrong, a dihydroxy derivative, was formed initially. The validity of Armstrong's mechanism was also brought into question by the work of Bone and Andrew (*8*), who showed, in the study of the oxidation of acetylene, that water was not essential to hydrocarbon oxidations.

The outstanding mechanisms among the many that have been proposed for the oxidation of the paraffin hydrocarbons are the hydroxylation theory and the peroxide theory. The hydroxylation theory is unconvincing because primary alcohols appear not to be primary products of hydrocarbon oxidation. The peroxide theory satisfactorily explains the prominence of aldehydes among oxidation products, but it cannot be considered proved fully because of the failure to isolate and identify peroxidic oxidation products; nor does it present a complete explanation of knocking, for the tendency of hydrocarbons to knock does not parallel what is known of their ability to form peroxides. From a study of flame propagation and radiation it is apparent that knocking accompanies a lack of smoothness in fuel combustion. Assumption of a chain mechanism for hydrocarbon oxidation makes intelligible the checking of knocking by chemical reagents which act as inhibitors of a special type. Such a mechanism also accords with the stimulation of knocking by unstable reactive substances. In the engine cylinder these may include oxides of nitrogen and ozone, as well as peroxides.

In his study of the alkyl benzenes Stephens (*55*) came to the conclusion that the alcohol stage was not intermediate in the oxidation of the side chains. He believed that the oxidation of the paraffin hydrocarbons took the same course as the oxidation of aliphatic side chains of aromatic molecules. As an important clue to the mechanism of these reactions, he stressed the fact that water retarded the oxidation of both the side chains and the paraffin hydrocarbons. For this he contended it was impossible to give any simple explanation on the basis of the hydroxylation theory. He proposed an oxidation mechanism which involved the union of a hydrocarbon molecule with oxygen to form a complex which split to give water and an unsaturated oxygenated residue. The formation of water as a primary product accounted for its retarding influence. The unsaturated residue was then assumed to rearrange to an aldehyde or ketone.

After the aldehyde stage, the steps in the oxidation of the lower paraffins are fairly clear and probably accord closely with the mechanism postulated by Bone and his collaborators. The aldehyde is oxidized further or is decomposed. Thus formaldehyde may be converted into formic acid or may split into carbon monoxide and water. Higher aldehydes, in addition, produce lower hydrocarbons, both saturated and unsaturated, which in turn undergo further change. The composition of the product of any given oxidation process is therefore the resultant of a considerable number of simultaneous reactions, proceeding at rates determined by the temperature and any catalysts which may be present.

It may well be that the oxidation of a gaseous paraffin hydrocarbon does not always pass through the same steps. Perhaps the primary alcohol, when formed, does not originate in the series of reactions which produces the aldehyde. Oxidation has been brought about by diverse methods—by direct heating with air or oxygen, alone or in the presence of catalysts; by contact with ozone; by reaction with oxidizing agents, holding oxygen in chemical combination, in solid, liquid, or gas phase; by the action of bacteria; or by the action of oxygen, while subjected to radiation from radioactive substances. Since the products obtained are not always alike, it is reasonable to suppose that the course of reaction may differ according to the method used. Particularly the oxidation under alpha radiation, studied by Lind and Bardwell (*46*), seems unlike other types of oxidation. These workers suppose that in this case, as a preliminary to reaction, "clusters" made up of gaseous hydrocarbon ions with oxygen molecules form. With methane and ethane the oxidation then proceeds to carbon dioxide and water, apparently in one step, while with propane and butane it is more complex, as intermediate products are formed. Further work is needed, however, to prove whether or not a hydrocarbon can oxidize by more than one route.

Catalysts should not affect the mechanism of hydrocarbon oxidation, though they may profoundly affect the products which can be isolated. Thus Wheeler and Blair (*60*) found that when the oxidation of methane was uncatalyzed it gave measurable amounts of formaldehyde, while with catalysts this compound could not be detected. They write:

> This is not surprising. The formaldehyde produced in our circulation experiments is in a concentration much greater than that given by the equilibrium $H_2 + CO \rightleftharpoons HCHO$. The rapid cooling enables it to be isolated before equilibrium is attained or further oxidation can occur. But with catalysts the true equilibrium is obtained almost instantaneously at the temperatures necessary to oxidize methane. The composition of the final gas, however, leads us to believe that catalysts do not change the course of the oxidation of methane and that with very high rates of gas passage some formaldehyde might be detected in the exit gases.

The Peroxide Theory

From the often conflicting mass of theory and experimental data which has been summarized, one fact is quite clear—the predominant product of the early stages of oxidation of a paraffin hydrocarbon is the aldehyde. But before the aldehyde appears, the formation of an intermediate product by the direct addition of a molecule of oxygen to a molecule of hydrocarbon is postulated by many present-day workers. Such an addition compound is termed by Grün, Ulbrich, and Wirth (*35*) a "moloxide," and is thought to be of the nature of an unstable peroxide. The development of a peroxide theory was forecast by Harries (*37*), who with little experimental evidence supposed that the reaction of ozone with saturated hydrocarbons went through the formation of a labile peroxide. The theory in its present form has developed from the great amount of work which has been done on the oxidation of the liquid paraffins in endeavors to account for motor knocking and to explain the efficacy of antiknock reagents. But if valid for the liquid hydrocarbons, the peroxide theory should hold equally for the gaseous members of this series. The evidence for the peroxide mechanism consists mainly in the finding by a number of investigators of a very active form of oxygen during the oxidation of hydrocarbons. They have attributed the activity of this oxygen to its being a part of peroxidic compounds, drawing an analogy from the oxidations of aromatic aldehydes, which have been proved to go through a peroxide stage. No peroxides, however, have actually been isolated as products of the oxidation of saturated hydrocarbons, though their formation has often been indicated. Bach (*3*) a number of years ago reported the formation of peroxides in the slow oxidation of "petroleum." After extensive work in this field, Callendar (*17*) wrote:

> Of the intermediate products of oxidation of the paraffins (hexane and above) the aldehydes were far the most important, reaching 70 per cent in the case of hexane. The first appearance of the aldehydes at low temperature was accompanied by a certain proportion of carbon dioxide and water. This led to the conclusion that the aldehydes themselves were decomposition products of some prior compound formed by the direct union of oxygen with the molecule of the fuel. The primary compound would probably be of a very unstable character and difficult to detect* * * The test for peroxides in the products of slow oxidation was immediately successful in the case of all detonating fuels.

Among these fuels were included the saturated hydrocarbons from pentane to undecane. The amount of peroxide or active oxygen formed increased in ascending the series.

Mardles (*48*) reports active oxygen in hexane-air mixtures after passage through hot tubes. He supports the peroxide theory because he believes that it offers an explanation of engine knocking, which the hydroxylation theory, he states, does not. Bäckström (*5*) writes:

> We have reason to believe that all oxidation reactions occur in two steps, the first oxidation product being a peroxide. Sometimes the peroxide accumulates in the liquid during the course of the oxidation; in other cases * * * the second reaction is so rapid that the peroxide disappears as fast as formed.

Berl, Heise, and Winnacker (*7*) suggest that in hydrocarbon oxidation dehydrogenation precedes peroxide formation. Loss of two atoms of hydrogen from the same carbon atom is thought to give a free radical, which becomes a peroxide by combining with a molecule of oxygen.

Egerton (*26*) does not believe that the peroxide intermediate in hydrocarbon oxidation is necessarily a "stable" peroxide. He supposes that a fuel molecule when heated first gains sufficient energy to unite with an "energetic" oxygen molecule. The result of this union is what he terms a "temporary" peroxide, which may revert to a normal state and form a stable peroxide or may break up again to give products in a highly active condition. One of these products will be the aldehyde. The essential step in the oxidation is therefore the formation of this temporary peroxide, the stable peroxide being more or less a secondary product. Whether the tests relied on to show the presence of peroxides in hydrocarbon oxidation indicate such temporary peroxides, or whether the stable form must result before it shows itself by chemical tests, is not certain.

Brunner and Rideal (*16*) found that in the oxidation of hexane an induction period preceded active combustion. The change in the character of the reaction after this induction period they attributed to the accumulation of peroxides. Measurements of the amounts of active oxygen present led them to the conclusion that peroxides equivalent to 3.2 per cent of the hexane present existed in the reacting material.

Lewis (*45*) sharply criticized the peroxide theory. He stated that Callendar's work was inconclusive because it did not show the actual formation of peroxides from the paraffin hydrocarbons. He claimed that Callendar's tests for active oxygen may have indicated the presence of hydrogen peroxide or, if they really showed organic peroxides, these may have come from unsaturated hydrocarbons derived from the paraffins and not from the saturated hydrocarbons themselves. Hydrogen peroxide has, in fact, been reported in the flames of illuminating gas (*32*), coke-oven gas (*53*), and hydrogen (*38*).

As an alternative to the peroxide theory, Lewis postulated the direct reaction of the hydrogen of a hydrocarbon with oxygen to form water and an unsaturated hydrocarbon. From the unsaturate thus produced he thought that aldehydes and peroxides might later form. Lewis believed that this view was preferable to the peroxide theory, because he found that at the moment of reaction an increase in the total number of molecules in the system occurred, whereas the peroxide mechanism would necessitate a decrease. He noted, as bearing on the knock problem, that cracked spirits, although containing peroxide-forming compounds, do not knock. He suggested that antiknock reagents prevent the dehydrogenation to an olefin, which is the first step in his oxidation mechanism.

Influence of Antiknock Reagents on Oxidation

When antiknock reagents are present in a hydrocarbon liquid undergoing autoxidation, usually no test for "peroxides" or active oxygen can be obtained. Moreover, the addition of organic peroxides to motor fuel increases its tendency to knock. Bennett and Mardles (*6*) report that lead tetraethyl and iron carbonyl appear to inhibit peroxide formation during slow combustion and that they raise the ignition temperatures of hydrocarbons and other fuels. Callendar (*18*) found that the addition of benzoyl or acetyl peroxide had a pronounced effect in inducing detonation. For these reasons motor knocking has been attributed to peroxide formation during combustion.

It may be questioned, however, whether the peroxide theory, or indeed any mechanism of oxidation as yet proposed, using mechanism as denoting a succession of intermediate products formed as steps in the oxidation process, is able to explain motor knocking. Certainly the earlier theories do not account for it; nor is the peroxide theory without contradictions. Against peroxide formation as the fundamental cause of knocking stands the fact that, although unsaturated hydrocarbons are non-knocking fuels, unsaturated compounds have, in general, a pronounced tendency to form peroxides. Although peroxides may be a factor in knocking, their formation does not seem a sufficient cause of this phenomenon.

Moureau, Dufraisse, and Chaux (*51*) related knocking with autoxidation and the formation of peroxides. Their work presents good evidence of the autoxidation of hydrocarbon materials with the simultaneous formation of compounds containing active oxygen, but there are some difficulties in applying their results to the explanation of knocking. In the autoxidation of a series of fractions of Pechelbronn petroleum the largest formation of peroxides was found in the lowest fraction, while the higher ones, which would be expected to be the worst knockers, gave doubtful or negative tests. Moreover, deca- and tetra-hydro-naphthalene showed pronounced autoxidation and formation of peroxides, although these substances belong to classes of hydrocarbons which are usually non-detonating in an engine. In endeavors to determine whether peroxides are formed in engine combustion, these workers found active oxygen in two cases, but could not obtain consistent results.

Other Phenomena Related to the Mechanism of Oxidation

But in considering oxidation mechanism, particularly as it concerns motor operation, attention must be paid to more than the identification of the substances formed during the process. Such phenomena as the propagation of flame and flame radiation are intimately related to the mechanism of oxidation, and of importance to the study both of oxidation per se and of oxidation as related to engine knocking.

Engine knocking has been thought to be synonymous with the detonation which is a late stage in the inflammation of a gas mixture of proper proportion in a confined space. Such detonation is a long-recognized and well-established occurrence. The great amount of work which has been done on this and other aspects of rapid combustion has been summarized by Clark and Thee (*23*) and by Garner (*34*). Recent studies of combustion have shown, however, that gas detonation and engine knocking are not the same thing. Egerton and Gates (*29*) consider that only in extreme cases is knocking due to a real detonation wave, as they could not produce true detonation in mixtures having a composition similar to those used in motors. Brown and Watkins (*15*) state: "The detonation wave as recognized in progressive homogeneous reactions is not a cause of 'detonation' (fuel knock) in internal-combustion engines."

Yet even though knocking and non-knocking combustion in engine cylinders are not so unlike as the uniform burning and the detonation observed as stages of gaseous explosion in tubes, study of the burning gases in engine cylinders has shown distinct differences between flame propagation during the normal operation of a motor and when knocking occurs. Egerton and Gates (*30*) associated knocking with a vibratory type of combustion and reported that lead tetraethyl tends to maintain but delay flame propagation. Maxwell and Wheeler (*49*) found that during knocking incomplete combustion occurred in the flame front and after a time a vibrating, accelerating combustion began, which on reaching the end of the cylinder originated a shock wave that caused violent explosion of unburned material throughout the vessel. Very small amounts of an antiknock reagent "eliminated the shock wave and tended to produce a continuous combustion in the wake of the initial flame." The picture is thus one of unruly combustion, a partial burning outrunning the remainder and causing finally a violent liberation of energy.

The evidence from the study of flame radiation accords with this point of view. Clark and Henne (*22, 21, 24*) studied the spectra of flames in an engine cylinder during non-knocking and knocking operations, taking four photographs during each combustion period. During the normal operation of the motor the radiation from the four quarters was much alike both in wave length and intensity. But when knocking occurred the spectrum of the first quarter was intense and extended far into the ultra-violet, followed by a great diminution in the succeeding portions. A "brutal" liberation of energy was indicated, almost all of it appearing in the first quarter of the stroke. On the addition of an antiknock reagent such as tetraethyl lead, the combustion regained the spectrum of normal combustion. Lead lines appeared only during the early part of the combustion, indicating that the action of the antiknock took place near the outset of the combustion.

> A true antiknock material shortens the ultra-violet spectrum and causes a uniform movement and reaction during the whole stroke, instead of the violent reaction during the first and to a lesser extent, the second quarter.

The antiknock substance thus slows down the reaction when it becomes overvigorous.

Apparently then, during knocking the oxidation or some component reaction "runs away," becoming so rapid that the combustion changes in character. Why change occurs may possibly be explained by a fuller knowledge of the steps through which the oxidation goes as revealed by chemical studies of oxidation. But more likely the reason why some fuels knock and others do not is to be sought in the more fundamental properties of the substances than the steps by which they oxidize.

Hydrocarbon Oxidations as Chain Reactions

A further consideration in regard to oxidation mechanism which appears to cast light on the action of antiknocks is the recently developed theory of chain reactions. Hydrocarbon oxidations are considered by a number of workers to have a chain mechanism. The term "chain reaction" designates a class of chemical change whose peculiarities are explained by assuming a special type of reaction propagation. A few activated molecules are thought to react, passing on to other molecules sufficient energy to activate them in turn and cause their interaction. Thus "chains" of reacting molecules arise, as assumed by Christiansen (*20*), Bäckström (*4, 1*), and their co-workers.

The two main characteristics of hydrocarbon oxidations which cause them to be classed as chain reactions are their tendency to autoxidation and the pronounced effect of inhibitors. These phenomena also accompany the oxidation of aldehydes, vegetable oils, and rubber, to which theories involving chain mechanisms have been applied quite successfully. The hypothesis that hydrocarbon oxidations are chain reactions does not, of course, depend upon the assumption of any specific series of products as intermediates, and its validity is therefore not conditioned upon the acceptance of any theory of oxidation.

The autoxidation of paraffin hydrocarbons at low temperatures is checked by many of the usual oxidation inhibitors, such as hydroquinone and the aromatic amines. Antiknock reagents have somewhat the same action. To some extent they retard oxidation at temperatures below ignition, and even in traces they stop engine knocking, much as small amounts of oxidation inhibitors stop slow oxidation. For this reason a number of investigators have included knock suppressors among oxidation inhibitors.

In some work, however, a difference has been found between the action of antiknock reagents and antioxidants. Moureau, Dufraisse, and Chaux (*51*) reported that at 160° C. certain antioxidants such as α,α- and β,β-dinaphthylamine, and hydroquinone markedly checked the autoxidation of paraffin and of the fraction boiling below 85° C. of Pechelbronn petroleum, but that lead tetraethyl or other knock suppressors retarded the autoxidation very little. The α,α-dinaphthylamine in a concentration of 1 per cent checked the autoxidation on a petroleum fraction almost entirely, while tetraethyl lead in the same concentration produced less than a 50 per cent reduction in reaction speed. In checking the oxidation of paraffin this proportion of dinaphthylamine had twelve times the effectiveness of an equal amount of tetraethyl lead. One per cent of tetraethyl lead reduced the rate of reaction but one-half while even in the proportion of one to one thousand, the amine slowed the oxidation to five per cent of its usual rate.

Similarly Layng and Youker (*44*) found that their tests on the inhibition of autoxidation failed to correspond with results on the checking of engine knocking. Experiments with diphenylamine showed that, in comparison with tetraethyl lead, in the gas phase, the amine had one hundred times the effectiveness as an oxidation inhibitor which it possessed as an antiknock reagent. Even 1 per cent of the lead compound did not affect the oxidation, although a fraction of a per cent is an efficient antiknock. A distinction should be made, therefore, between oxidation inhibitors, which under conditions of slow reaction greatly retard oxidation or stop it entirely, and antiknock "dopes," which are not particularly effective at low temperatures but markedly change the character of combustion.

A Mechanism of Knock Suppression

The following is offered as a possible explanation of this differentiation which should be made between substances that inhibit slow oxidation and those that stop knocking.

The oxidations inhibited by antioxidants normally proceed under nearly constant conditions of temperature and pressure, and when not inhibited proceed at a constant rate. The amount of energy passed along a chain of molecules may be considered as about constant. According to current theory, this amount of energy, if transmitted, probably by collision, to one or more molecules of an antioxidant is sufficient to bring it into reaction. The oxidation of the inhibitor dissipates energy and breaks the hydrocarbon oxidation chain (*1*). If sufficient antioxidant is present, practically all of the hydrocarbon oxidation chains are broken and the amount of reaction that occurs becomes infinitesimal.

In the cylinder of an internal-combustion engine the oxidation reaction occurs at an accelerated rate and at constantly increasing temperature. The energy passing down a reaction chain under these conditions may be thought to increase continually in amount. Suppose that in the early stages of combustion the majority of molecules possess such low energy that collision with a molecule of a knock suppressor, such as lead tetraethyl, has no effect either to oxidize or to decompose it. The oxidation chain reaction will go on unchecked. This is consistent with the failure of knock suppressors to stop the autoxidation of hydrocarbons at comparatively low temperatures. However, as oxidation goes on, the temperature rises and the molecules pass on more and more energy. If this process goes on unchecked, the shock wave and surge of radiation characteristic of knocking will be developed. But before this occurs a critical point is reached at which sufficient energy is transmitted by a reacting molecule to a molecule of knock suppressor to cause either its dissociation or the oxidation of an already dissociated fragment. The reaction chain is then broken, not at the start, but when it has reached a certain high energy condition. Perhaps only the molecules reacting in one of the steps in the oxidation acquire sufficient energy to affect the antiknock, and it is the checking of a part-reaction that prevents uneven burning and knocking. Not all molecular chains would have the same energy content at a given time.

Even when oxidation occurs below the ignition point, some molecules may attain the critical energy content. By picking out these high energy chains—"hot molecules" as Christiansen (*20*) termed them—the knock suppressor, while not greatly retarding low-temperature oxidation, would delay inflammation, or at least render it more difficult. This view is in accord with the findings of Egerton and Gates (*28*), Weerman (*59*), and Berl, Heise, and Winnacker (*7*) that the addition of knock suppressors raises the ignition temperature of hydrocarbons and their oxidation products. An antiknock substance, on this basis, is an oxidation inhibitor of special type. It does not greatly change slow oxidation, but checks its undue acceleration.

Moureau, Dufraisse, and Chaux (*51*) explained the comparative ineffectiveness of lead tetraethyl in low-temperature autoxidation as due to easy oxidation. More likely the lack of effect should be attributed to difficulty of oxidation, to the hydrocarbon molecules being oxidized possessing too little energy to bring the antiknock into reaction. From the work of Charch, Mack, and Boord (*19*) it is apparent that the most effective metallic antiknocks, including lead tetraethyl, are not readily oxidized by air.

The hypothesis that antiknock reagents can act only on reaction chains of high energy should be equally applicable, in the case of metallic derivatives, whether they act as organic compounds or only after decomposition to give particles of finely divided metal.

While Egerton (*27*) did not make a special classification of knock suppressors, he assumed a chain reaction for hydrocarbon oxidation, considered that these substances were effective by breaking chains, and postulated "regions of high energy, containing molecules in high energy states" as an accompaniment of knocking. "Antiknocks, by inhibiting the processes of combustion, which occur in those centers, are therefore effective in preventing knocking."

Causes and Aids of Knocking

It has been shown conclusively that, when introduced into an engine cylinder, unstable and reactive substances, such as organic peroxides, alkyl nitrites, and nitrogen peroxide (*48*), cause intensified knocking. To peroxides formed during combustion has therefore been attributed the incidence of this phenomenon. But it is entirely possible that other active substances besides peroxides are produced in a motor and occasion knocking. The most probable of these are ozone and oxides of nitrogen.

Ozone has been found in hydrocarbon flames (*47*, *56*) and, as shown by the many investigators cited by Rideal (*52*), it is formed on raising air or oxygen to a high temperature, though readily again decomposed. Hofmann and Kronenberg (*39*) have shown that the combustion of coal gas or acetylene can be so regulated that ozone is formed in sufficient amount to be very easily recognized by its odor at some distance from the flame. Jones and Parker (*41*) obtained appreciable quantities of nitrogen oxides in both the slow combustion and the explosion methods of gas analysis. Haber and Coates (*36*) found nitric oxide in the combustion of carbon monoxide, its formation being aided by increased pressure. Yant (*62*) has established the presence of oxides of nitrogen in the exhaust gases from gasoline engines. In view of the admitted influence of active substances as knock inducers and their effectiveness in small quantities, it is entirely reasonable to suppose that ozone and nitrogen oxides may be present during engine combustion in amounts sufficient to be a primary cause of knocking.

This supposition is made more probable if a chain mechanism is accepted, as those reactions to which the chain mechanism theory has been applied with apparent success are highly sensitive to accelerators and are stimulated by minute amounts of activators. Active substances such as ozone and nitrogen oxides would tend to set up centers of high energy and give rise to active fuel molecules, which would start an increased number of reaction chains, accelerate the combustion, and bring about the sudden evolution of energy that accompanies knocking.

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Inflammability of Mixtures of Ethyl Alcohol, Benzene Furfural, and Acetone[1,2]

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THE lower limits of inflammability of the vapors of ethyl alcohol, benzene, and acetone have been determined by a number of investigators (*2*), but no information was available for mixtures of these solvents and for furfural when mixed with them. This report gives the results obtained on the lower limits of inflammability of mixtures of the solvents ethyl alcohol, benzene, furfural, and acetone. The tests were carried out jointly with the Westinghouse Electric and Manufacturing Company, of East Pittsburgh, Pa., and were made only on those solvent mixtures in which that firm is particularly interested. The information was desired in connection with the development of ovens for the removal of solvents from various materials. Although the results are limited to the mixtures mentioned, the data should be of value to other industries which may have similar problems.

Apparatus

The apparatus used for determining the limits of inflammability is similar to that described in previous publications (*1*, *4*), but modified for use at higher temperatures as shown in Figure 1. In its operation air is introduced through a drying tower, *a*, passed through the T-piece *b* and flowmeter *e*, thence to the vaporizer *p*. The T-piece dips under water to a depth which can be regulated as required and serves to maintain constant rates of flow of the gases through the flowmeter by acting as a relief valve for excess of air. The flowmeter is calibrated by a standardized wet meter at one point to give a rate of one liter per minute. The air flow is maintained at this rate throughout the experiments.

The solvents are introduced into the air stream through the vaporizer *p* from the reservoir *t*. The rate of introduction is regulated by the rate of admission of water to reservoir *u* from the constant rate device *w*, described in previous reports. The vaporizer *p* is heated by a surrounding coil of nichrome wire, the amount of heating being controlled by a slide-wire resistance. The solvent-air mixture then passes to the top of the explosion tube *r* as shown. This tube is 5 feet (1.5 meters) in length and 2 inches (5 cm.) in diameter. The mixture then passes down this tube and out at the bottom. A funnel surrounds the bottom of the tube, which in turn is connected to a canister containing activated charcoal, and an exhaust pump that removes the vapors after leaving the apparatus. The explosion tube *r* and connecting tube leading to the vaporizer are wound with nichrome resistance wire and covered with asbestos to maintain the gases at an elevated temperature. Three spaces, *d*, are left in the explosion tube, as shown, for observation of the flame passing up the tube. In the tests given the temperature of the explosion tube was maintained at 125° C. at the lower part, while the upper part of the tube was 10 to 15 degrees hotter. A close control of the temperature is not important because the limits of inflammability are not appreciably affected by small changes in temperature; the primary idea of heating the tube was to prevent the sol-

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[2] Published by permission of the Director, U. S. Bureau of Mines. (Not subject to copyright.)

[3] Associate chemist, U. S. Bureau of Mines, Pittsburgh, Pa.

[4] Chemist, Westinghouse Electric & Manufacturing Co., East Pittsburgh, Pa.

vents (furfural mixtures) from condensing out after leaving the vaporizer and also to approximate the temperature usually encountered in the ovens.

Test Procedure

The solvent from a previous test is removed from the apparatus by turning cock *m* clockwise and lowering mercury seal *g*. The mercury and solvent then flow out of the right-hand branch of cock *m*. The reservoir *t* and all connections are then thoroughly washed, first with alcohol and then ether, and then dried by aspirating with dried air. Cock *m* is then turned to connect *t* with *u*. Mercury is then added to *u* until reservoir *t* is filled, the test solvent then poured into *y*, mercury seal *g* lowered, and mercury drained out at *v*. In this way the mercury level in *t* falls, drawing in the solvent from *y*. When bulb *t* is about two-thirds full of the solvent, discharge tube *v* is closed and mercury seal *g* is raised, and the apparatus is ready for use. The air rate is adjusted to give a flow of one liter per minute, the vaporizer and explosion tube are heated to the desired temperature, the ground-glass plate *s* covering the bottom of the explosion tube *r* is slid to one side allowing a small opening for the gases to escape, and the exhaust pump is started to remove the vapors discharged from the explosion tube. The reservoir *w* is filled with water and adjusted to such a height that the discharge rate of water through the jet *x* is sufficient to give a discharge rate of the solvent into the vaporizer somewhere near the inflammable limit. If the height of *w* above *x* is not changed, the dropping rate of water into tube *u* will be constant. The dropping rate (drops per minute) is checked with a stop watch and when found constant the air-solvent mixture is passed through the explosion tube for 15 minutes.

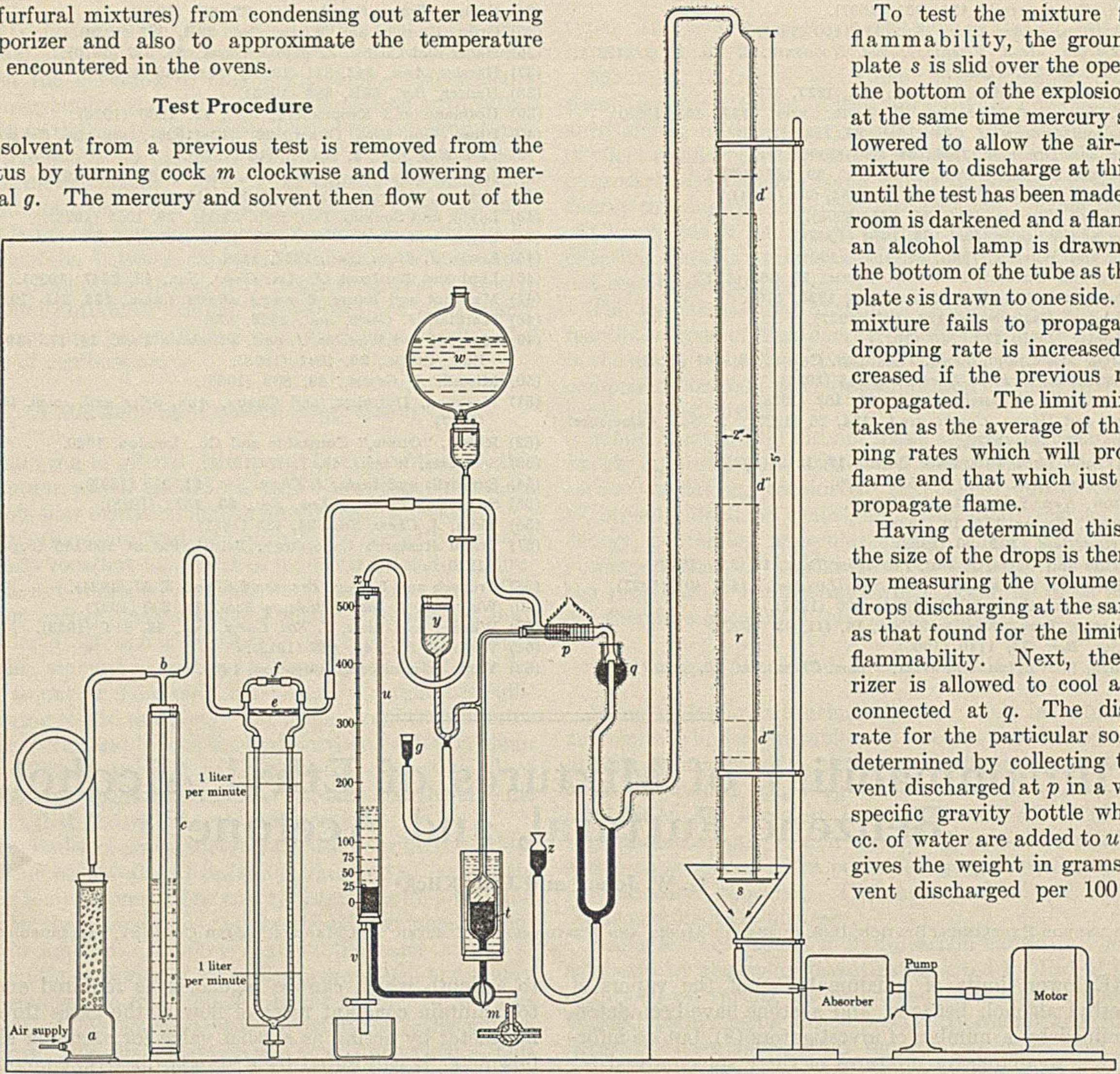

Figure 1—Inflammability Limits Apparatus for Mixed Gases and Vapors

To test the mixture for inflammability, the ground-glass plate *s* is slid over the opening at the bottom of the explosion tube, at the same time mercury seal *z* is lowered to allow the air-solvent mixture to discharge at this point until the test has been made. The room is darkened and a flame from an alcohol lamp is drawn across the bottom of the tube as the glass plate *s* is drawn to one side. If the mixture fails to propagate, the dropping rate is increased, or decreased if the previous mixture propagated. The limit mixture is taken as the average of the dropping rates which will propagate flame and that which just fails to propagate flame.

Having determined this value, the size of the drops is then found by measuring the volume of 100 drops discharging at the same rate as that found for the limit of inflammability. Next, the vaporizer is allowed to cool and disconnected at *q*. The discharge rate for the particular solvent is determined by collecting the solvent discharged at *p* in a weighed specific gravity bottle when 100 cc. of water are added to *u*. This gives the weight in grams of solvent discharged per 100 grams of water. Knowing the volume of the drops of water, the number per minute to give the inflammable limit, the discharge rate per 100 cc. of water, the temperature and pressure of the room in which the tests are made, and the molecular weight of the solvent, the limit of inflammability can be calculated.

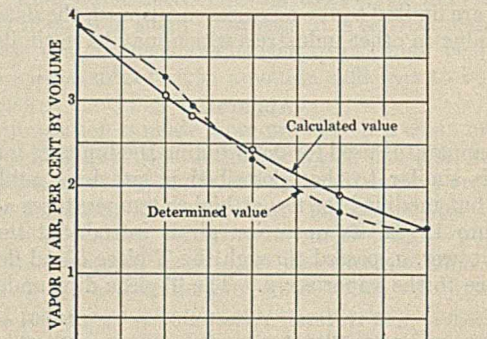

Figure 2—Agreement between Determined and Calculated Lower Limit Values for Mixtures of Benzene and Alcohol Mixtures

In using this method it is assumed that one gram-molecule of the solvent gives 22.4 liters of vapor at 0° C. and 760 mm. Hg. It is known, however, that vapors do not obey the laws for a perfect gas, especially at higher pressures; however, as the concentrations of the vapor in the mixtures are low (below 4 per cent), this error should not be large.

The composition of various mixtures of solvents tested and their lower inflammable limits as determined by experiment, are given in Table I. All values are for temperatures of 125° C. and the prevailing atmospheric pressure, 740 mm. Hg average.

Table I—Inflammability of Solvents

TEST MIXTURE	COMPOSITION OF TEST MIXTURE (PER CENT BY WEIGHT)				LOWER INFLAMMABLE LIMIT (PER CENT BY VOLUME)	
	Ethyl alcohol	Benzene	Furfural	Acetone	Detd.	Calcd.
	%	%	%	%	%	%
1	100.0	...	...	...	3.85	3.85
2	75.0	25.0	...	...	3.30	3.06
3	67.0	33.0	...	...	2.99	2.84
4	50.0	50.0	...	...	2.30	2.44
5	25.0	75.0	...	...	1.72	1.94
6	...	100.0	...	...	1.53	1.53
7	...	...	100.0	...	2.10	2.10
8	75.0	...	25.0	...	3.52	3.44
9	25.0	...	75.0	...	2.69	2.57
10	...	...	...	100.0*	2.92	2.92
10a	...	...	...	100.0	3.18	3.18
11	80.0	...	...	20.0	3.76	3.71

SPECIFICATIONS OF SOLVENTS USED

Ethyl alcohol—S. D. No. 1, boiling point 76° to 80° C., sp. gr. 0.817, contains 5 per cent H_2O.

Benzene—Boiling point 78° to 82° C., sp. gr. 0.882.

Furfural—Boiling point 161° C., sp. gr. 1.159.

*Acetone—Chemically pure, boiling point 55° to 57° C.

Acetone—Commercial, boiling range 3.7 per cent below 54° C.; 59.5 per cent from 54° to 56° C.; 30.7 per cent from 56° to 60° C.; and 6.1 per cent from 60° to 68° C.

The limits of inflammability of the mixtures of solvents have been calculated by the use of LeChatelier's law (*3*), and as given in the table show a maximum variation between calculated and determined values of 0.24 per cent. Figure 2 shows graphically the lower limits of inflammability of ethyl alcohol–benzene mixtures both by determination in the apparatus previously described and as calculated by LeChatelier's law. Although the variations between calculated and determined values are not large and almost within the experimental error, still it appears that the addition of benzene to ethyl alcohol in proportions from zero to about 50 per cent raises the limit of inflammability of the mixture above that obtained by calculation, and when the proportions of benzene are in excess the determined values are lower than the calculated values.

Conclusions

The lower inflammable limits found for the solvents when mixed with air and at 125° C. were as follows: ethyl alcohol, 3.85 per cent; benzene, 1.53 per cent; furfural, 2.10 per cent; acetone (C. P.), 2.92 per cent; and commercial acetone, 3.18 per cent.

The results of tests made on various mixtures of these four solvents give limits of inflammability (lower) when mixed with air, which agreed closely to calculated values obtained by the application of LeChatelier's law.

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Iodine Numbers of Lubricating Oils before and after Use in Automobile Engines[1]

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LUBRICATING oils are commonly regarded as stable organic compounds consisting of cyclic saturated and unsaturated hydrocarbons. Comparatively high temperatures and great pressures are required to bring about any extensive structural changes in this class of compounds. It is not generally realized that such conditions are present in all gas engines when in use. The breaking down of oils under high pressures has been observed and recorded, even when bearings were so well cooled by special devices that no local heating could have taken place. The present investigation was undertaken with these facts in mind and with the object of determining what structural decomposition, if any, occurs in oils when used as lubricants in automobile engines. The fact was not overlooked that a change in the oil as a whole might be brought about by the absorption of unsaturated compounds out of the gasoline, which compounds, through polymerization, might give rise to lubricating products. In any case, the amount of such substances formed must be very small, as it is just these unsaturated compounds that are oxidized most readily and thus removed as gaseous products.

The determination of the iodine number of an oil before and after use affords a ready means of determining the amount of structural change undergone. It has been shown that in order to obtain concordant results for iodine absorption, a prescribed method (*7*) must be followed exactly. The suggestion has been made (*1*) that work should be done at lower temperatures than previously, thereby to retard substitution and produce more consistent results. Consequently, all these reactions were allowed to take place at the temperature of melting ice (*4*). No claim is made that the results indicate unsaturation only, as it is quite possible that some substitution took place even at this temperature. Since differences only were desired, the above method was deemed to be sufficiently accurate for the purpose, and all measurements were reproducible.

Procedure

The procedure was essentially that due to Hübl (*3*) with important modification suggested by Wijs (*9*), which is detailed below. The acetic acid used was redistilled with a little potassium permanganate to oxidize any alcohol or acetaldehyde. It was tested for any oxidizable substance by heating with potassium bichromate and concentrated sulfuric acid until, after standing, no green tinge was noticeable. Thirteen grams of pure iodine were dissolved in 1 liter of glacial acetic acid (99 per cent). Washed and dried chlorine was then passed into the solution until the color changed from dark brown to reddish yellow. It was then allowed to stand 24 hours and kept in the dark. A slight excess of iodine is preferable. It was standardized with sodium thiosulfate (*5*),

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[1] Received January 17, 1929.

which in turn was standardized by Volhard's method. Carbon tetrachloride was used as a solvent, as preferable to chloroform, and this was tested in a similar manner to that of acetic acid above. A 10 per cent solution of potassium iodide was used, and kept in the dark; also a freshly prepared 1 per cent starch solution. The Pyrex flasks were of 250 cc. capacity with well-ground glass stoppers. These were cleaned before each run with a strong solution of alcoholic soda and dried.

The factors known to influence the iodine number are the weight of oil taken, the excess of iodine present, the temperature, and the time of absorption (*7*).

A definite amount (0.35 gram) of dried oil was placed in the flask, dissolved in 10 cc. of carbon tetrachloride, and 25 cc. of the iodine monochloride solution added. This volume made the excess of iodine approximately 90 per cent. The flask was then surrounded with melting ice and placed in the dark for exactly 2 hours. Lewkowitsch recommends $^1/_2$ hour for the completion of the reaction at room temperatures, which was found equivalent to 2 hours at 0° C. After 2 hours 20 cc. of potassium iodide solution and 100 cc. of water were added. Great precautions were taken to prevent loss of iodine by volatilization, the liquids being allowed to run around the wide-lipped neck about the stopper, which was partially removed to allow the solution to enter the flask. The excess iodine was titrated with thiosulfate, using starch indicator at the end. The method was tested with oleic acid, which gave a value of 90.91, while theory predicts 90.07. This agrees very well with that found by Wijs (*9*) of 87.6 with his own solution, and that of Geitel of 89, using Hübl's solution.

SAMPLING—The old oil was drained off from the car in which it was to be tested and the crankcase flushed out with a small amount of the desired lubricant. After this had been removed, the car was filled and a sample of the original oil retained for examination. Sufficient oil was also placed in a separate container so that the same oil could be added from time to time to maintain the oil level. After a certain definite mileage a sample of the lubricant was removed and its iodine number determined. A large number of different cars were used, all of them late models in good mechanical condition. Some were equipped with oil filters and ventilated crankcases.

The diluent was not removed, as there exists at present no method by means of which the heavier ends of gasoline can be completely separated from the lubricating oil. The effect in general is to raise the iodine number of the oil, owing to the large amounts of unsaturated compounds in the gasoline. An idea as to the change brought about by dilution can be gained from the following figures, which were obtained by determining the iodine number of an oil before and after dilution with ordinary gasoline to such an extent that the viscosity of the mixture was equal to that of the oil removed from the car:

OIL	IODINE NUMBER BEFORE DILUTION	IODINE NUMBER AFTER DILUTION	INCREASE IN IODINE NUMBER
21	17.3	18.6	1.3
57	29.0	30.4	1.4
31	29.2	29.3	0.1

All samples of oil were carefully dried over pure anhydrous calcium chloride for one week, with frequent shaking. To assure the absence of minute particles of calcium chloride, and to separate all dirt and sludge from the oil, each sample was centrifuged before use and the clear oil removed by decantation. No evidence was obtained that the calcium chloride exerted a selective action on the oils.

Results

The results are given in the accompanying table. The results show that in nearly all cases the iodine number decreases in spite of dilution. Oils 28, 29, and 59 appear to be exceptions. Excessive dilution was noticeable in No. 28, but not in the others. It is also of interest to note that the decrease is greatest during the first 500 miles. Oils 35 and 57 were used in cars equipped with oil filters, but no abnormal change was found in the oil. Several explanations can be brought forward to account for the decrease of the iodine number. Thus, the unsaturated hydrocarbons, being more easily oxidized than the saturated, are removed during combustion by conversion into gaseous products, or they may be only partially oxidized to form the insoluble sludge and removed by precipitation. Further investigation should decide this point.

Iodine Numbers of Lubricating Oils before and after Use in Automobile Engines

OIL	TYPE OF OIL	MILES COVERED WITH OIL IN CAR	INITIAL IODINE NUMBER[a]	FINAL IODINE NUMBER[a]	DECREASE IN IODINE NUMBER
1	Medium	500	20.9	20.1	0.7
2	Medium	1000	...	19.8	1.0
3	Medium	1500	...	20.1	0.7
4	Heavy	600	44.2	42.8	1.3
5	Medium	700	29.0	28.5	0.4
6	Medium	1500	40.4	37.8	2.6
7	Medium	600	14.9	14.7	0.2
8	Medium	1000	...	14.3	0.5
9	Medium	500	30.5	29.7	0.8
10	Medium	500	43.4	42.4	1.0
11	Medium	1000	...	41.9	1.5
12	Medium	500	28.9	29.6	−0.6
13	Medium	1000	...	29.1	−0.1
14	Medium	500	41.7	39.5	2.1
15	Medium	1000	...	38.2	3.5
16	Medium	500	47.3	45.3	2.0
17	Medium	550	45.1	43.1	1.9
18	Medium	1000	...	41.3	3.8
19	Heavy	500	22.5	22.4	0.1
20	Heavy	1000	...	23.6	1.1
21	Medium	500	17.3	18.3	−0.9
22	Medium	500	23.5	21.1	2.4
23	Medium	500	16.6	15.4	1.1
24	Medium	500	36.3	35.9	0.4
25	Medium	1000	...	37.6	1.0
26	Heavy	500	22.7	19.1	2.6
27	Heavy	1000	...	21.1	1.6
28	Heavy	1000	22.9	28.8	−5.9
29	Heavy	1500	39.0	40.5	−1.5
30	Medium	500	29.1	21.7	1.4
31	Medium	1000	...	17.0	12.1
32	Medium	500	28.9	25.9	2.9
33	Heavy	500	23.9	16.6	7.3
34	Heavy	1000	...	14.2	9.7
35	Heavy	500	39.3	38.4	0.9
36	Heavy	1000	...	38.8	0.4
37	Heavy	500	39.0	37.8	1.1
38	Heavy	1000	...	37.2	1.7
39	Heavy	500	23.4	21.5	1.8
40	Heavy	1000	...	20.7	2.6
41	Medium	500	18.9	16.7	2.1
42	Medium	1000	...	19.8	1.0
43	Medium	500	44.2	43.4	0.7
44	Medium	1000	...	41.7	2.4
45	Medium	800	19.1	17.0	2.0
46	Medium	800	36.9	35.1	1.7
47	Medium	500	18.4	16.2	2.2
48	Medium	1000	...	15.5	2.9
49	Heavy	600	40.7	39.5	1.2
50	Medium	500	23.1	21.7	1.4
51	Medium	250	22.3	20.4	1.8
52	Medium	800	...	22.0	0.2
53	Medium	600	25.4	24.4	0.9
54	Medium	500	21.3	19.7	1.6
55	Medium	500	21.0	20.0	1.0
56	Medium	900	24.5	23.0	1.5
57	Medium	500	28.9	27.6	1.3
58	Medium	1000	...	28.4	0.5
59	Medium	500	23.5	25.1	−1.5[b]
60	Medium	500	22.2	22.0	0.1
61	Medium	1000	...	22.8	−0.6

[a] Averages of two determinations which in no case varied more than 2.5 per cent.

[b] Negative signs mean increase in iodine number.

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Rapid-Indicating Continuous-Reading Vacuum and Pressure Gages[1]

H. G. Anderson

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Two gages have been developed for measuring pressures continuously and at high speeds. These gages will withstand a change of pressure from atmospheric to zero without injury. Pressure measurements are made almost instantly. The No. 2 gage has a comparatively high sensitivity for pressures between 20 and 1 mm. or below. With the exception of the three positions for pointer movements across the scale of the No. 2 gage, no manipulations are required during a course of measurements. A separate calibration is required for each gas. The gages, being rugged, do not require skilled hands in using them.

THE engineering development and manufacture of products involving exhaust have presented problems in pressure measurement which have proved the inadequacy of the gages customarily used for this purpose (*2*, *4*). The particular problem of measuring the exhausting speeds of various kinds of pumps first focused our attention upon the development of a gage suitable for making measurements continuously and at relatively high speeds. From this the development was expanded to include advantages in covering other requirements more suitably than with other gages. Two hot-wire gages have been devised, each of which is adapted to particular needs.

The gage most commonly used has been the McLeod gage, in which a volume of gas is compressed within a capillary tube and the pressure determined from the difference in heights of two mercury columns. Considerable time is required to exhaust the capillary tube each time before a pressure reading is taken. Since there is a length of tubing to connect the gage with the pump, another lag is introduced, in the speed at which the gage obtains the vacuum produced at the pump or chamber whose pressure is being measured. The McLeod gage, furthermore, is only useful in taking pressures at the instant the volume of gas to be compressed in the gage is cut off from the system whose pressure is being measured. In the study of present-day exhaust equipment it is often desirable to take a measurement in 5 seconds or less. The McLeod gage is entirely unsuited for such work.

Ionization gages have been tried, but they did not yield complete satisfaction. It is necessary to have some auxiliary gage to assure that the pressure is low enough to permit using the ionization gage. Without this assurance there is danger of injuring the gage. Then, too, a considerable amount of apparatus is required to make up a gage of this sort. This gage, moreover, is adaptable only to pressures approaching the order of complete vacuums. It does, however, have the desirable feature of giving a continuous indication of pressure change.

The next gage that was tried was a type of hot-wire gage made up as a thermojunction. This gage came the nearest to embodying the various features which are desired in the measurements of pressures connected with low-pressure or vacuum devices. It comprised a somewhat delicate meter, which did not make it well suited to use on a factory floor. This gage has a certain amount of lag due to the small length of heated wire used and to the relatively large amount of metal within the thermojunction tube, the temperature of which will influence that of the junction. For instance, if the circuit were left open while the exhaust of a bulb was taking place and then closed, 17 seconds or thereabouts would elapse before the meter pointer came to rest.

The usual arrangement of the Pirani bulb hot-wire gage (*3*, *5*) was then set up. A calibration was made between pressure and voltage required to maintain a constant current in the filament. This method required that manipulation be made during the course of measurements of a range of pressures, and was therefore a cumbersome process. The development from this point was the design of a gage in which no manipulations were required in recording the change in pressure throughout the range from atmospheric pressure down to 0.25 micron or less. The principle of operation, the design of the bulbs and the electrical circuits, the calibrations, and the applications of these gages will now be described.

Principle of Operation

From the kinetic theory of gases we know that the heat conductivity of a gas changes with its pressure. With a substantially uniform heat supply to the filament, the varying amount of heat taken away by conduction from the filament when there is a change in the gas pressure causes a change in the temperature of the filament. The filament, being platinum and consequently having different resistances at various temperatures, changes in resistance when the gas pressure varies. This change of resistance disturbs the balance in a Wheatstone bridge into which the bulb is introduced when making a measurement of pressure. This change of balance is recorded on a meter and in this way a visual indication of the pressure occurring at any instant in the exhaust system is maintained.

Design of Bulbs

For convenience one of these gages is designated the No. 1 gage and the other the No. 2 gage.

The bulbs which have been devised for these gages are made of heavy-walled hard glass to withstand breakage and to avoid disturbances from sudden momentary changes of temperature.

The filament is in the form of a thin ribbon, which provides a surface of contact with the surrounding gas four times as great as would be had from a round wire with the same area of cross section. By this means heat energy put into the filament is quickly imparted to the gas. If the gas pressure is low, around 100 microns, a small change in pressure affects appreciably the amount of heat that will be conducted away by the gas. As the gas pressure decreases the gage becomes more sensitive; as it is increased the sensitivity becomes less.

The bulb for the No. 1 gage contains a single filament. The filament length is such that the resistance, with a given

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[1] Received March 22, 1929.

current flowing in it, is the same as that of another filament mounted in a similar bulb and taken as an arbitrary standard. In this way bulbs are made with a fixed amount of resistance; hence they give the same reading for a given pressure.

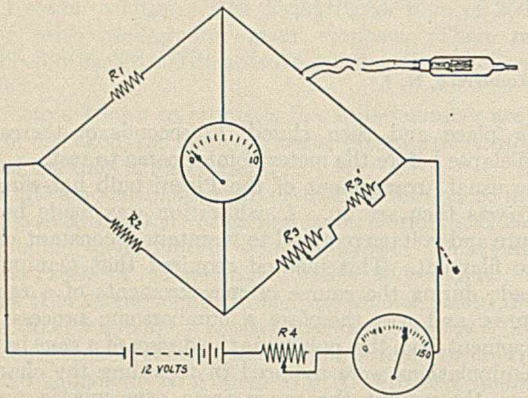


Figure 1—Electrical Circuit for the No. 1 Hot-Wire Gage

The ends of the calibrated length of the filament are spot-welded between strips of nickel ribbon. The strips are in turn spot-welded to the lead-in wires. The supports over which the filament is draped are drawn up taut to make a firm contact between the filament and the support, thereby avoiding fluctuations in cooling by varying contact with the support. This bulb in use dissipates about $^1/_3$ watt.

The bulbs for the No. 2 gage contain two parallel filaments. Each filament is supported so as to occupy one-half the space about the axis of the bulb. The parallel filaments are employed to increase the amount of energy to be dissipated. The sensitivity of the bulb is increased for higher gas pressures if the energy to be conducted away is increased.

Electrical Circuits

No. 1 Gage—Figure 1 shows the electrical circuit for the No. 1 gage. This gage is best suited for measurements of pressures between 0.25 mm. and 0.25 micron or less, but will withstand pressures up to atmospheric. *R*1 and *R*2 are made approximately equal. *R*3 and *R*3' together equal the resistance of the bulb when the bulb is open to atmosphere and the designated current flowing through the bridge current meter. *R*4 is used to set the bridge current.

To operate the gage set the bridge current by adjusting *R*4 with the bulb open to atmosphere. At the same time adjust the *R*3 resistance until the 0–10 milliampere meter pointer rests at zero. Then place the bulb in the system whose pressure is to be measured. At first the pointer drops backward as a result of cooling from the expansion of the gas. Gradually the needle will begin to rise and move continuously until the lowest pressure is reached. If the electrical circuit is left open during the exhaust and is then closed, the pointer will rise and come to rest in about 6 seconds, indicating that this gage operates nearly three times as fast as the thermojunction gage mentioned above.

The amount of the full scale which is covered by the pointer during the change of pressure from atmospheric to 0.25 micron is governed by the bridge current used. Figure 4 includes a calibration for this gage. It can be seen from the curve that very little error will be introduced from fluctuations in the atmospheric condition from one day to another by using this method of establishing the zero setting. As the zero setting is made for the atmospheric temperature at the time the measurement is made, it is not so necessary to employ a temperature-compensating bulb in the bridge circuit. Since the bulb is required to dissipate so little energy, its temperature does not rise perceptibly above that of the surrounding atmosphere. Therefore, moderate disturbances of the atmosphere about the bulb do not affect the usefulness of the pressure measurements. The resultant bridge resistance increases as the pressure decreases, causing a drop in the current flowing through the bridge. No adjustment is made for this drop, since if the battery is kept at a uniform charge this drop will be constant.

No. 2 Gage—Figure 2 is the electrical circuit for the No. 2 gage. This gage covers the same range of pressure measurements as the No. 1 gage, but the pressure-indicating meter pointer is made to move across the meter scale twice in the range of pressure change which causes the pointer of the No. 1 gage meter to move approximately one-fifth of one passage over the meter scale. This added sensitiveness in the higher pressure range is derived from supplying more heat energy to the filaments. The energy to be dissipated from one of these bulbs is sufficient to make it noticeably warm to the touch. The bulbs are made larger than those for the No. 1 gage to assist in the release of energy. Notwithstanding this, compensations (*6*) must be made for probable fluctuations in the temperature of the air surrounding the bulb.

Two compensator bulbs are used in this gage. They are mounted on the back of the gage and are exposed to the atmosphere. One is brought into play when making measurements covered by the first and second movements of the pointer across the meter scale, the other is used when measuring pressures covered by the third movement across the scale.

The resistance at contact point 4 is introduced in the circuit for the first movement across the scale, in order to avoid too great a complexity of compensator bulbs. The point of rest for the meter needle when the bulb is open to the atmosphere will vary with the atmospheric conditions. For this reason a different method of setting the bridge current must be adopted.

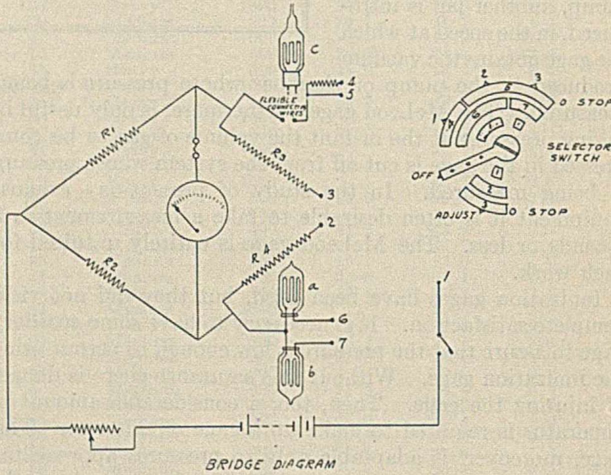


Figure 2—Electrical Circuit for the No. 2 Hot-Wire Gage

The design of this gage comprises a means of setting the bridge current whereby the pressure-indicating meter becomes the current-setting meter. Resistances *R*3 and *R*4, constituting an auxiliary Wheatstone bridge, are contained within the gage. All the resistances are of wire having a low temperature coefficient of resistance. They are wound non-inductively. The resistances of the two branches replacing the bulbs are made substantially the same as those of the respective bulbs when in operation. One is made enough larger than the other so that the pointer will come to rest at a specified reading when the proper bridge current is reached. For the sake of more accurate measurements it is desirable that the battery be kept at about the same point of charge for this gage as well as for the No. 1 gage. The effective resistance of the bridge for either gage increases as the pressure decreases. Unless the resistance by which the bridge current is adjusted is practically the same at all times, the voltage drop across the resistance will vary when the voltage of the battery varies and thereby create an error in the pressure indication.

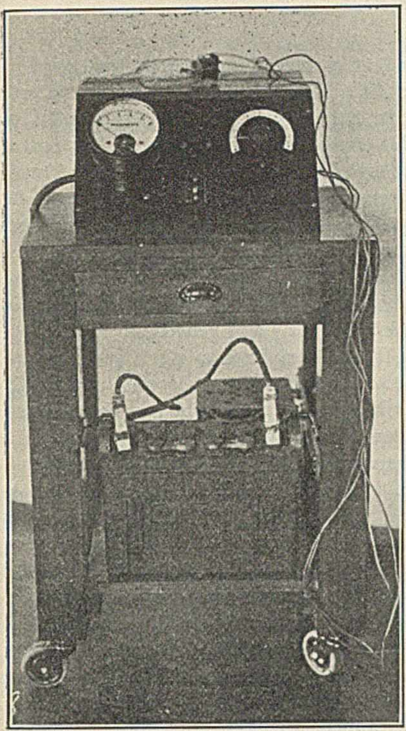


Figure 3—Front View of No. 2 Gage Mounted on Table

To simplify the operation of this No. 2 gage, the special selector switch shown in Figure 2 was devised. By means of this switch it is possible to join the various contact points in the proper sequence when covering the different pressure ranges or when setting the bridge current. It will be noted that the lugs marked 1 cover a shorter arc, so that other contacts are certain to be made before the battery circuit is closed. Without this precaution a current several times greater than the capacity of the milliammeter would be forced through it. A fuse is provided in the circuit in series with the milliammeter to protect this meter in case of accident, such as an unintentional breaking of the circuit to the measuring tube.

Mounting

The meters or meter, depending upon whether it is a No. 1 or a No. 2 gage, are mounted on a sloping panel front of a box within which the bridge resistance and wiring are placed. Adjustments are made through knobs mounted on the panel. The sloping panel affords easy observations, making it possible for one or more persons to observe the pressure. Figure 3 is a photograph of the front view of the No. 2 gage. The box can be mounted on the top of a small rugged table which is supplied with large rubber-tired castors. The storage battery required to supply the constant voltage, together with its charger, is supported on the lower shelf. The whole device can be readily moved about a factory floor. Another desirable form is a portable one which can be carried from place to place. This includes the box part only, the battery being provided separately.

Calibrations

Figure 4 shows the calibrations of the two gages for dry air, omitting that portion below one micron. A separate calibration (*1*) is required for each gas whose pressure is to be measured. This necessitates also that the kind of gas be known. The calibrations were made when using a mercury diffusion pump for exhausting. No liquid air was used to trap extraneous vapors. The calibrations are shown for scale divisions traversed. One hundred divisions comprise a full scale. Since there must be some overlap on the successive pointer movements across the scale, the three movements do not cover three hundred divisions on the No. 2 gage. The particular range covered can be marked off once the amounts of the overlaps are established.

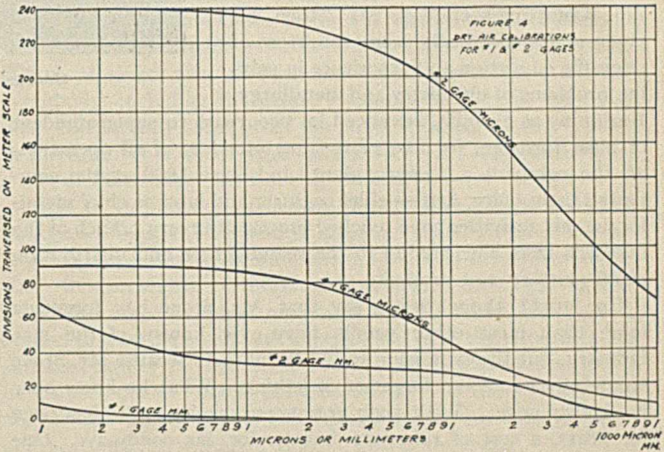
A glance at the curves shows that the sensitivity of the two gages is nearly the same for pressures below 150 microns. Above that pressure the No. 2 gage has an increasingly greater sensitivity. For a pressure of 1 mm. the No. 2 gage is approximately nine times as sensitive as the No. 1 gage. For a pressure of 30 mm. the No. 2 gage has the same sensitivity as a U-column mercury gage. At 1 mm. the No. 2 gage is seventy times as sensitive as the U-column mercury gage.

Uses

From the original use of measuring the exhaust speed of pumps, more than a score of uses have been found for these gages. The bulbs can be tabulated in various ways to add to the conveniences to be had from them. These forms permit placing the bulb anywhere in a machine. Long flexible leads from the box to the bulb allow making continuous readings around an indexing or revolving machine. Since the bulb is glass, it can be sealed directly into a glass exhaust system.

The fact that the gage embodies no volatile matter makes it particularly useful in measurements where extraneous gases would be a hindrance.

These gages are very rugged and are not easily injured. There are more than a score of these gages in use in our plants. None of them have required more than minor repairs. In case bulbs become fouled they can be quickly cleaned. One objection to the McLeod gage is the difficulty of cleaning, especially where exhaust over mercury diffusion pumps is being measured.



Where a higher sensitivity is required in the region approaching a complete vacuum, it will be found advisable to reverse the movement of the pointer and make the higher meter reading correspond with the higher pressure. Then when the pressure is reduced to a few microns the 0–10 milliammeter can be replaced with a microammeter and the measurements continued on that meter. Such an adaptation could readily be made in a laboratory.

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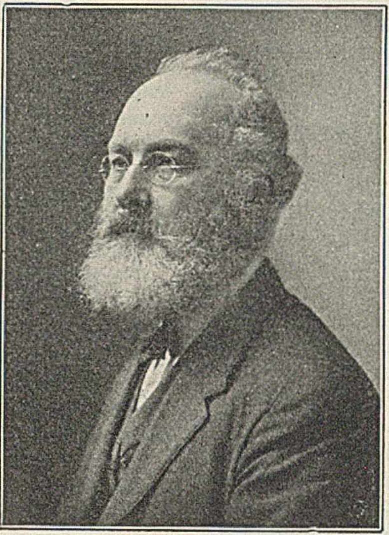
AMERICAN CONTEMPORARIES

George C. Stone

Among his acquaintances the mention of the name of Mr. Stone brings to mind a character and figure quite outside the ordinary. Imagine the head of Queen Victoria's Lord Salisbury with white hair and a white bushy beard. Picture a man with well-built, supple frame and ease of movement, clothed in loose-fitting British tweeds. Give him a gravity of bearing which is heightened by a pair of gold spectacles and lightened by the smoke of an ever present cigarette, and you have a sketchy outline of Mr. Stone in his seventieth year. Strange though it may seem, his portrait if taken today would be almost an exact likeness of Mr. Stone at forty-five. In character and disposition no less than in outward appearance he is the same today as he was twenty-five years ago, a serene and quiet student and scholar, rarely ruffled, rarely excited, pretty firmly convinced that there is little new under the sun.

He came to The New Jersey Zinc Company in 1882 with the background of his studies and his graduation at the Columbia School of Mines followed by three years' work as a wage-earner in the practice of chemistry. For forty-seven years in the Zinc Company's employ, Mr. Stone has given of his constantly increasing store of scientific education and experience in solving problems of chemistry and metallurgy. Beginning as chemist, advanced in two years to superintendent of blast furnaces, for five years superintendent of all operations of the company's Newark plant, and since 1900 at the company's main office, first as chief engineer and later as chief metallurgist, his activities have touched practically every branch of the industry from zinc mining to the manufacture and distribution of all primary zinc products.


George C. Stone

One might thoughtlessly say that Mr. Stone has forgotten more than most other people have ever known of the zinc industry, but the expression would be inexact, because Mr. Stone seems never to have forgotten anything. What he knew once he knows now. With such equipment he is, as he has been for years, a sort of reference bureau for his company. One of his colleagues, himself a man of great learning, once remarked that "Mr. Stone comes nearer to being a human encyclopedia than any other man I ever knew." Another of the Zinc Company's officials, stationed at a somewhat remote plant, said he particularly valued Mr. Stone's visits because when one was far from a great scientific library the lack of opportunity to consult such an institution could largely be remedied by opportunity to confer with Mr. Stone. These illustrations are the more apt because, like the reference library, Mr. Stone must be applied to if one wishes to tap his store of knowledge. Modest, almost to a fault, it is not characteristic of him to thrust his wares upon those who do not seek them. For those who ask he is ready and generous.

It is a privilege to work with and to be with a gentleman so learned and kindly as Mr. Stone. While he can be firm and even abrupt with one who persists in a theory which practice has proved unsound, he is sure to be patience itself in discussing with juniors any problem which is new to them or which, by some rare chance, may be new to him. Nobody who merely seeks the truth need fear to consult him; but, as was once said of a noted leader in the zinc business, "if you don't want his opinion you'd best not ask it."

Eminent as Mr. Stone has become in science as applied to zinc metallurgy, he has also, like many deep students, distinguished himself in an avocation in which he has sought the intellectual refreshment of an outside interest. Mr. Stone's avocation or hobby is a somewhat unusual one. It consists of collecting ancient armor and arms. So long and diligently and with such discrimination has he been devoting his leisure hours to this specialty that his collection is now the finest and most complete outside those in public museums. In fact, a large number of his treasures are now placed at the Metropolitan Museum in New York City.

Mr. Stone, in the practice of his profession, has traveled far and wide. Australia, Africa, much of Europe, and many of the remote parts of North America have been touched by his itineraries. His journeys have yielded great gains to his fund of knowledge. He still proceeds sturdily and persistently to accumulate knowledge and armor specimens. He bids fair to continue for a score of years. His many friends hope that he will.

H. S. Wardner

Research on Cold-Working of Steel

A new laboratory for research on the cold-working of steel has just been opened at Sheffield University, Sheffield, England. It has been established with the aid of a generous gift from the Iron Mongers' Company, of London, which has made a grant of approximately $4000 a year for seven years to endow a fellowship and two scholarships.

The firms connected with the cold-working industry have, through the Cutlers' Company, presented the necessary plant. The mechanical equipment includes a wire- and bar-drawing machine. By means of a two-speed gear and variable-speed motor, wire-drawing speeds of from 28 to 360 feet a minute may be obtained and wires can be drawn of all sizes up to $^3/_8$ inch in diameter, and rods up to 1 inch diameter.

The rolling plant has hardened steel rolls 10 inches in diameter and 10 inches in face and is fitted with two-speed gear box and variable-speed motor, giving a range of rolling speeds from 52 to 319 feet a minute. The lubrication is by a patent flood system. Water cooling is provided for the rolls and roll bearings and for the oil in connection with the lubrication system.

NOTES AND CORRESPONDENCE

Passing the Patent Office Buck

CRITICIZING the Patent Office is a favorite sport in the best chemical circles. Everybody's doing it. I do it myself sometimes when an examiner does not agree with my views on chemistry, a recurrent phenomenon which always puzzles and irritates me. Between times, however, I realize that it is just as useful to fuss about the Weather Bureau.

And as I like to be fair in odd years and this is 1929, I shall pass the buck for the Patent Office, or at least translocate it somewhat; and then ask you to tell your troubles to a Senator.

Mainly what ails the Patent Office is what ails the rest of us patent people—the lack of an authoritative, modern body of case law on which to base reasoning and opinion. Case law there is in plenty, but the decisions are either not modern or not authoritative.

Up to 1891 patent litigation went to the Supreme Court for final adjudication just as any other litigation did. The nineteenth century gave us a host of new ideas, wonderful then and commonplace now. Each was duly patented and many were bitterly litigated, with the litigation winding up in the Supreme Court. In a general way the Court looked at all legal questions from the viewpoint of law rather than equity; holding that, a patent being the creature of statute, patentees were entitled to their statutory rights, neither more nor less. The Court took the letter of the statute and the letter of a man's claims. If his wording was unfortunate, that was his bad luck. It was hard practice; but it had the advantage of being definite, logical, and consistent. And it had the greatest virtue of all, finality.

Then Congress created a lot of Circuit Courts of Appeal, making the decision of each in patent matters final in its own circuit, but not controlling in any other. Appeals to the Supreme Court were cut out. Since patents are national and not local, I have never been quite able to see the beauty of subdividing an adjudication of validity into fractions. And I understand there are patent owners who find it inconvenient and expensive to try validity over and over again in different circuits. At first in patent matters the Courts of Appeal all followed Supreme Court decisions, then recent and controlling; but as time went on these decisions became antiquated and new questions arising were handled on new lines, with a tendency to do equity rather than try law. Gradually the several courts, being wholly independent, veered apart and in patent matters each has established its own view of the law. Today a man trying a patent case in any circuit is well advised if he relies mainly on the decisions rendered in that circuit. In other words, so far as case law of patents is concerned, there are nine kinds in the country now and, as a tenth circuit has just been created, presently there will be ten kinds. Once in a while when the courts range too far apart patent cases go to the Supreme Court by certiorari, and then we do have a decision which is final and which clears the air on some point. But these certiorari cases are too few to affect the general situation much.

Meanwhile the Patent Office keeps on doing business at the old stand mostly, practicing under nineteenth century decisions and applying the letter of the law to the letter of the claims as the Supreme Court used to do it. And when a court man from a circuit using two-point-five statute law interviews an examiner who tips his hat when he passes a shelf of Supreme Court reports, there is profound bewilderment on both sides. I act as interpreter occasionally.

The Patent Office is an institution; but it is also a group of men whose contact with the public they serve is more individual than collective. There are some 600 examiners, all educated men, mostly liking their jobs and all hard at work under inconvenient conditions in two old buildings crowded with old papers. Of clerical assistance they have little, nor is much possible. The 600 are organized into 62 examining divisions, among which are distributed the 308 classes that embrace all knowledge. Each division is a complete and self-contained autonomous unit headed by a primary examiner and equipped with a clerk and a stenographer. It has no connection with any other division and it does business directly with applicants for patent as long as an application is under examination. Within the division, in turn, there are a number of assistant examiners, each working independently, examining the class, or fraction of a class, assigned to him. Team work is mostly out of the question. All of which amounts to saying that the Patent Office is really an association of 600 non-competitive specialists. And the 600 average just as various and just as human as any other bunch of 600 college graduates, recent and not so recent.

There is an enormous turnover in the junior grades of assistant examiners, young college graduates spending a year or so in the Office and then resigning. Primary examiners rarely change. Better salaries on the outside are a factor in this turnover, but only one factor. There are a hundred other reasons, 99 of them working, why a young chap may think it looks pleasanter outside than inside. Office conditions play their part. When I left, which was some time ago, it was because of a difference of opinion: the Office thought it was up to me to examine leather-working machinery and I didn't agree. The constant parade of green men through the examining corps is hard on everybody, including the primary examiners and not excluding me. But broadly considering the public interest, however, maybe the turnover is worth while since the Patent Office has become a sort of Plattsburg school for the industries.

Some of the difficulties in the Patent Office are mechanical, owing to the expanding field of search. When I was in the examining corps, the patent numbers ran between 700,000 and 800,000. The present numbers run as high as 1,700,000. So my successor has twice as many references to keep in mind as I had. It used to take me about half a day to leaf over the patents in one subclass, that of "Evaporating Pans." It takes him longer unless he looks quicker. Each examiner today, on the average, has about 7000 United States and foreign patents to keep in mind; and next year he will have more. This is too many.

What can be done about the expanding field of search I don't know; nor does anybody else. It is self-evident that examiners must depend more and more on indexes and digests and less on actual searching. And I might venture to suggest that concerns aggrieved by the appearance of what they think new patents on old things would display an intelligent self-interest by sharing their tabloided information with the Patent Office.

I had the further advantage over my successors in that I had a certain sweet certitude as to what to do with a reference when I found it. Not only was the Supreme Court body of case law recent and controlling, but "the practice" in the Office was fixed and standardized. The "Rules of Practice" were then intended to be followed. There was a distinction between "merits," which meant mostly novelty, and "form," which meant everything else in the "Rules of Practice." From a "rejection" on the merits an appeal lay, first to a board of examiners-in-chief and then to the

Commissioner. From an "objection" to form an interlocutory petition, for which no fee was charged, went to the Commissioner directly. Petitions were filed in flocks every day and the Commissioner's hand was in every division. Any examiner or attorney with aberrant ideas was soon whipped into line by the umpire. The result of the system of objections and petitions was wholesome. Everybody had to live up to the Rules and "the practice" was uniform.

Interlocutory petitions to the Commissioner on miscellaneous matters of practice, however, became obsolete in 1903 with the Supreme Court decision in the Steinmetz case (109 O.G. 549). With that decision, as the Commissioner reacted to it, most of the things we thought matters of "form" became matters of "merit" and objections and petitions were no longer in order. The Commissioner could no longer be reached directly and his powers as an umpire between examiner and attorney went into the discard. Everything had to be dealt with by appeal. For a time a system of piecemeal appeal was tried, but it was too much of a nuisance and it has been dropped. The net result was that the Commissioner lost practically all his supervisory power, as distinguished from his judicial power.

To recapitulate, the Patent Office is really in the situation of the sheep when Bo-Peep was lost. It has no modern body of law which it can or will use. I have had primary examiners, and not the worst in the bunch, tell me that they pay no attention to court decisions because they "vary so much." It has had no internal uniformity in practice since *ex rel.* Steinmetz appeared and tied the hands of the Commissioner, making the "Rules of Practice" a relic. It is really 62 independent patent offices, each going its own way and with its own individual practice, and each struggling with a constant expansion of its work and with a succession of green assistant examiners. It is a surprise to me that the 62 do as well as they do.

Coming back to my text, while I shall acknowledge the truth of criticisms of the Patent Office and indeed I could sing some songs of sorrow of my own, yet I want to point out that the difficulty really lies with Congress and not with the Patent Office. I recommend that, instead of throwing bricks, an effort be made to have Congress (1) restore the supervisory authority of the Commissioner in the Patent Office and (2) create a central court of patent appeals to which all patent cases can be appealed, ridding us of the present chaos. This will not only save money, work, and time to patentees, but it will give the Patent Office a body of consistent case law on which it can rely and by which it is bound.

Incidentally, somebody will then be able to write a textbook of patent law.

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July 3, 1929

BOOK REVIEWS

The Pyrolysis of Carbon Compounds. By Charles Dewitt Hurd. A. C. S. Monograph 50. 807 pages. The Chemical Catalog Company, Inc., New York, 1929. Price, $12.50.

This monograph, written with two primary motives, "the provision of as complete a survey as possible of the pertinent literature, and the rational organization of this material," maintains the high standard set by previous books in the American Chemical Society monograph series, and fills an important need in chemical literature. The organic chemist will find an organized discussion covering all types of carbon compounds, presented in such a way that many interesting problems will suggest themselves. The physical chemist will see that his aid is needed in continuing the work on free energies and other physico-chemical methods of attack necessary for a quantitative study of the problems. The industrial chemist is given, not only a concise discussion of his particular field, with numerous references to recent literature, but also a general view of the theoretical background. It is to be regretted, however, that more emphasis was not placed upon the economic importance of pyrolysis in the petroleum industry; the automobile, a symbol of current life in America, could not have reached its present status if cracking were unknown.

The treatise begins with a discussion of general principles and concludes with a chapter summarizing pyrolytic polymerizations and depolymerizations. The intervening chapters contain descriptive matter arranged in logical order, beginning with hydrocarbons and running through all types of carbon compounds. As a literature review this monograph deserves high commendation. One great difficulty in compiling literature on pyrolytic reactions lies in the fact that very often they will not be indexed as such in the abstract journals. This situation is responsible for some omissions—for example, in the section on proteins. Then, too, a comprehensive summary of pyrolytic molecular rearrangements would have been of considerable interest, even though the general subject of rearrangements has been covered by another monograph in this series.

The more mechanical phases are in keeping with the general excellence of the rest of the book. The free use of structural formulas, including those of hypothetical intermediate compounds, is to be commended. Twenty-nine of the 64 tables are summaries of the behavior of certain groups of related compounds; these tables are of great aid in systematizing the data and in conserving space. The usage in compounding names of organic compounds is not rigorously uniform throughout the text. In a few isolated cases the danger of omitting the initials from the names of investigators was encountered, since work by two men has been placed under the same name in the author index.

The theoretical discussion in the introductory chapters should do much toward arousing interest in pyrolysis. The author's analogy between the water, ammonia, and methane systems should be of value in predicting qualitatively the course of reaction, and the study of the electron attraction of radicals should be of great interest from the quantitative standpoint. It is to be hoped that more studies will be made also in regard to thermodynamic relationships. The inclusion of theoretical discussions throughout the text, as well as the author's critical attitude, makes this monograph, which might easily have become a mere catalog of the literature, a valuable book from every point of view.—Lawrence W. Bass

Proceedings of the Second International Conference on Bituminous Coal, November 19–24, 1928. In two volumes. Volume I, 987 pages; Volume II, 940 pages. Published by Carnegie Institute of Technology, Pittsburgh, 1929. Price, $15.00.

The two volumes which report the proceedings of this conference give a very fitting résumé of one of the outstanding events in the field of coal utilization. Over one hundred manuscripts, supplemented by worthwhile discussion, present what is undoubtedly the most valuable treatise on present knowledge of coal preparation, burning, and processing.

Chemists who have occasion to look up the various schemes for low-temperature coking and the European practice for coal handling will especially welcome these volumes, since most of the commercial methods which have been recently developed, in both the United States and Europe, are treated by some representative of the promoting company.

If the reader will use in appropriate quantity the proverbial "grain of salt" in studying the economic significance as presented by the backers, he can count on this work as being an excellent guide. That there should be some discounting of the claims of the various advocates of processes is self-evident. However, this is a criticism neither of the advocate nor of the splendid conference from which these volumes have come. It is a natural and inevitable result of enthusiasm for a new method which leads to that degree of exaggeration which is noted in these particular papers. The remainder of the conference is most satisfactorily free from even this small occasion for criticism.—R. S. McBride

Infra-Red Analysis of Molecular Structure. By F. I. G. Rawlins and A. M. Taylor. 176 + xv pages. Cambridge University Press, Cambridge, England; The Macmillan Company, New York, 1929. Price, $3.50.

This book, which is one of the Cambridge Series of Physical Chemistry under the editorship of E. K. Rideal, comes as a particularly welcome addition to the literature, inasmuch as no book in English exists which deals with the application of infra-red spectroscopy to the analysis of molecular structure. The plan of the presentation consists of an interesting introduction by Doctor Rideal, a chapter on gases, one on liquids, one on solids, one entitled "Experimental," and a mathematical appendix. According to the authors, the theme is that of the interchange of energy between matter, gaseous, liquid and solid, and infra-red radiation. With the properties of such an energy they are but little concerned, which explains the omission that is of much interest in the verification of different radiation formulas and in the ramifications of pyrometry. The reader has a peculiar satisfaction in perusing the book because of the certain feeling that here is the last word on an important branch of molecular physics. It is impossible to see how a better presentation could be made, considering the fact that the subject is now in the most rapidly growing stage of its existence. A quiet optimism has crept into the pages of the book and yet the limitations are clearly and honestly set forth. These limitations are concerned, of course, with a lack of experimental data where technic is as difficult as is to be found anywhere in experimental science. The various chapters are excellently documented with references to original papers leading up nearly to the end of 1928. The book is free from error in spite of the large number of symbols, and the mechanical features are entirely satisfactory. The authors are to be congratulated and sincerely thanked for performing a genuine service for chemistry and physics in this monograph which has no competitors.—George L. Clark

Blood and Urine Chemistry. By R. B. A. and I. E. Gradwohl. 542 pages; 117 illustrations; 4 color plates. C. V. Mosby, St. Louis, 1929. Price, $10.00.

The authors' preface characterizes this work as a textbook designed for laboratory workers and practitioners of medicine. The reviewer, however, regards it as more of an extended laboratory manual—of immense practical value. It is obvious that the construction of the book has been discontinuous. Chiefly made up of details of laboratory performances, set forth clearly, and according to the authors "following a plan which we have used for a number of years in our instruction of laboratory technicians," it carries in addition considerable quoted material, in good sequence, yet giving to the book the unmistakable earmarks of an assembled work. The explanation of hydrogen-ion concentration, for instance, is exactly that published by a commercial house in its trade literature. The chapter on basal metabolism is quoted almost in its entirety, certain tables therein bearing the copyright of another commercial house. However, in spite of this tendency away from original effort, the work is quite complete. There is no book, at present, just like it, and it carries more worthwhile practical information than any other book of its kind.

The volume is divided into four main parts: The Technic of Blood Chemistry (155 pages); The Chemistry of Urine (which includes, oddly enough, a chapter on the bacteriologic examination of urine—73 pages); The Interpretation of Blood Chemical Findings (142 pages); and Basal Metabolism (74 pages).

The illustrations are, in the main, very useful, although some familiar and none-too-descriptive cuts are prevalent in the chapter on urine microscopy. The colored plates are more expensive than they are valuable.

Proof-reading and indexing have been well done, although the meticulous one would query the placing of myrtillin in the authors' index. In the compilation of chemicals and reagents appearing in the fore part of the book there is met that too frequently recurring unscientific *scientific* (?) performance—namely, the redundance of synonyms. For instance, here we meet *ethyl alcohol* where later it is *ethylic alcohol* and still later just *alcohol*.

The bibliographic references, which are numerous, are helpful, but beyond all it is the clarity of detail and the completeness of method in that part designed for the technician that gives this book its real value.—Ivor Griffith

Atlas der letzten Linien der wichtigsten Elemente. By F. Löwe. 44 pages. 16 pages of charts. 15 × 22 cm. Theodor Steinkopff, Leipzig, 1928.

This little book consists of two parts, the introduction and the atlas proper. The atlas lists the common elements alphabetically by symbols, giving for each element (*a*) the spectrum of the dry carbon electrodes, (*b*), (*c*), (*d*), (*e*) the spectra of various solutions of the element either alone or in combination, (*f*) a second spectrum of the carbon electrode, and (*g*) the wave-length scale of the spectrograph. On the page opposite each group of spectra is a list of the wave lengths to be expected. The atlas deals only with those lines which the author considers to be useful in chemical analysis. The atlas is followed by a table covering nine pages which would be very useful in the interpretation of the spectra of samples of unknown composition, if it were free from errors.

Unfortunately, this book is hardly up to the standard to be expected of the Zeiss Works. In some places the proof-reading has been poorly done. For example, on page 8 the author speaks of twenty-one elements, but the reviewers can only count twenty in the author's list. In the same sentence he includes Nd among the symbols of the "remaining fifteen elements" from the same list, but Nd is not in his original list. On pages 20 and 29 wave lengths are given, followed by the symbols Ag and Ni, respectively, with no accompanying Roman numeral; for the sake of consistency these symbols should be omitted if the degree of ionization is unknown. An error which illustrates the danger of compiling data from second-hand sources is brought out in the wave lengths given for phosphorus. These are taken from Kayser's "Tabellen der Hauptlinien" and are all high by 0.8 Å. Kayser evidently accepted the measurements of Saltmarsh in *Phil. Mag.*, **47**, 877 (1924), but failed to notice that he gives the wave lengths in vacuum instead of atmospheric pressure. The other wave lengths in the "Tabellen," as well as in nearly all other published tables, are given for atmospheric pressure.

In making the spectrograms the author has evidently used the older type of carbon electrodes instead of the modern, extremely pure electrodes, and the spectrograms, therefore, have more lines to be disregarded than is customary at present in this country.

All in all, this little book is a disappointment. It might have been a valuable book if it had been well done. Apparently it gives little information that has not appeared previously, and in better shape, in a number of places.—Wheeler P. Davey and Charles C. Nitchie

Die künstlichen Harze. By Johannes Scheiber and Kurt Sandig. Band XIV of Chemie in Einzeldarstellungen, edited by J. Schmidt. 376 pages. Wissenschaftliche Verlagsgesellschaft, M. B. H., Stuttgart, 1929. Price, bound, 28 marks; paper, 26 marks.

The theoretical portion of this latest book on synthetic resins is very well written and the literature relating to the theories underlying resinous condensations and polymerizations has been comprehensively collected and summarized. Practically every type of synthetic resin which is or has given promise of being of value is described and classified, and the possible mechanism of its formation discussed.

The authors' treatment of the practical application of the phenol-formaldehyde resins is not so satisfactory, however, and is far from up to date. Approximately ten pages, six of which are abstracted from the Bureau of Standards Technological Paper 216, that was published in 1922 and contains much obsolete material, suffice for a discussion of molded and laminated plastics, a subject in which enormous progress has been made in the last five years. The illustrations are meager and not very carefully selected.

Considerable space has been given to the urea resins, while the more important thiourea resins are practically neglected. The glyptal resins and the phenol-formaldehyde resins of the albertol type also have assumed increasing importance and deserve a fuller discussion.

The tests on electrical insulating materials included as an addendum are of interest in that they show the present European requirements.

The reviewer has noted few errors in the text, although the formula given on page 113 and attributed to Baekeland was only tentatively proposed by him and then later abandoned, while the statement in footnote 78, page 148, concerning ownership of the trade name "Glyptal" is obviously in error. Also he would question the statement on page 171 that the coumarone resins constitute the major portion of the three commonly used synthetic resins—namely, coumarone, aldehyde, and phenol-aldehyde resins. While a comparison of these is somewhat difficult owing to their widely varied applications, certainly the phenol-formaldehyde type is more extensively employed than any other, at least in the United States.

The book will prove, however, a welcome addition to the meager publications on the increasingly important subject of synthetic resins.—JOHN H. SCHMIDT

Diagramme und Tabellen zur Berechnung der Absorptions-Kaltemaschinen. BY FR. MERKEL AND FR. BOSNJAKOVIC. 43 pages with 30 figures and 4 plates of diagrams. Julius Springer, Berlin, 1929. Price, 12 marks.

This brochure is a technical-mathematical treatment of the heat exchange involved in refrigeration machines of the absorption type.

The contents of the book are arranged under three main divisions. Part I, by Merkel, treats of the mathematical calculations and is subdivided under the following heads: (1) Working of the Absorption Machine; (2) Operating Cycle; (3) Total Heat Balance of the Plant; (4) Heat Balance of the Generator and the Absorber; (5) Percentage Content of the Strong and Weak Aqua Ammonia; (6) Heat Balance of the Liquefier and the Evaporator; (7) Heat Exchanger; (8) Return Flow; (9) Countercurrent Exchanger between the Liquefier and the Evaporator; (10) Overlap of Temperatures; (11) Multiple-Stage Absorption Machine; (12) "Resorption" Refrigeration Machine; (13) Power Requirements of the Aqua Pump; (14) Temperatures; (15) A Typical Example; (16) Efficiency of Operation of the Installed Absorption Machine. Part II, by Bosnjakovic, consists of an exposition of the calculation and interpretation of the formulas and factors involved. Part III is a collection of twenty-eight tables supplemented by four large sheets of plotted curves contained in a pocket in the back cover.

Throughout the work there are numerous diagrams and curves accompanying the various mathematical calculations on heat transfers involved in the absorption system of mechanical refrigeration.

The book is handsomely printed and all the diagrams are beautifully clear notwithstanding the complexity of some of them. No doubt the work will prove to be a valuable contribution to the literature of the refrigeration industry.—CHARLES H. EHRENFELD

Von den Kohlen und den Mineralölen. Ein Jahrbuch für Chemie und Technik der Brennstoffe und Mineralöle. Band I—1928. 252 pages. Issued by the Division of Fuel and Mineral Oil Chemistry of the Verein Deutscher Chemiker. Verlag Chemie, G. m. b. H., Berlin, 1929. Price, paper, 15 marks; cloth, 17 marks.

This volume contains seventeen papers with discussions on fuel and mineral oil chemistry, presented at the annual meeting in Dresden of the Verein Deutscher Chemiker. In the introduction Spilker and Frank stress the present-day importance, not only of the production, transmission, and utilization of energy, but also its transformation. The chemist is especially concerned in the transformation of energy, as witnessed by his work in the conversion of coal into more flexible and more valuable forms of energy, such as gas, oil, and motor fuel.

The papers themselves cover a wide variety of subjects—high- and low-temperature carbonization, complete gasification, constitution and origin of coal, fusibility of coal ash, high- and low-temperature tars, synthetic oils, combustibility of coke, examination of coke-oven gases, refining oils with sulfur dioxide, and the determination of the aging tendencies of steam turbine and transformer oils.

American fuel technologists will be interested in Müller's comprehensive review of the present status of coal processing in Germany; in Rosin's scientific exposition of the properties and uses of low-temperature coke from brown coal and from bituminous coal; in Agda and Lyncker's contribution to the theory of coke formation; in Brückner's extensive report of his research on phenols in coal tar; and in Schuftan's comprehensive paper on the heavy hydrocarbons and other constituents not usually determined in coke-oven gas. Discussions are given at the end of each paper.

In general, the papers set a high standard of scientific and technical excellence, and most of them appear to be original contributions.—A. C. FIELDNER

Die Wandstärkenberechnung druckbeanspruchter Gefässe aus Schweissstahl-, Flussstahl-, Kupfer- und Aluminumblech im Apparatenbau. Monographien zur chemischen Apparatur, established by A. J. KIESER. BY HANS MELHARDT. 61 pages with 10 illustrations, 2 diagrams, 17 tables in text, and 15 insert sheets. Otto Spamer, Leipzig, 1929. Price, paper, 7 marks; bound, 8.50 marks.

In the introductory chapter the author contrasts the paucity of bases for calculations of the wall strengths of pressure vessels of sheet and plate steel, copper, or aluminum, with the profusion of formulas available for the ordinary shop practice and steam-boiler construction. This deficiency he undertakes to remedy by "a thorough study and extension" of available formulas, and by devising new ones. The formulas on which he leans particularly are those for steam-boiler construction, given in the official German "workshop and construction regulations for stationary steam boilers" of October, 1926, with supplements of April, 1927, and comments thereon published by the German steam-boiler interests.

The materials included are wrought iron, plate (soft) steel, copper, and aluminum; he considers welding by the gas torch and electric welding in addition to the older blacksmith or hammer weld. Hard and soft solder joints are studied and numerical values given. The shapes considered are spheres, half spheres, and sections of spheres, with radii up to 4000 mm., and cylinders up to 3000 mm. in diameter and for varying distances between points of support. The pressure range is up to 15 atmospheres. The insert tables are for rapid reading of wall thicknesses for given conditions.

The booklet will be welcomed in the engineering departments of firms which manufacture chemical apparatus, evaporators, autoclaves, cookers, or even mixing tanks. The information is very specific, which will make it all the more valuable in the comparatively few places where such information is essential. Special attention might be called to curves showing the decrease in strength of copper and aluminum with rise in temperature from 0° to 400° C., compiled from experimental values only partly taken from the literature.—E. RAYMOND RIEGEL

Chemische Nomogramme. Erste Sammlung: Nr. .001–.006. Published on the occasion of the "Dechema," Deutsche Gesellschaft für chemisches Apparatewesen. BY OTTO LIESCHE. Verlag Chemie, G. m. b. H., Berlin, 1929. Price, 2 marks.

This is a collection of six charts on heavy paper which are intended to facilitate certain calculations frequently required in commercial laboratories. Other charts will be issued as their need is indicated. This collection includes the following: 0.001, mixing; 0.002, density and degrees Baumé; 0.003, reduction of gas volume to standard conditions, weight of 1 cc. of nitrogen, vapor pressure of water at 5–26° C.; 0.004, per cent of sulfur from weight of $BaSO_4$; 0.005, per cent of phosphorus and P_2O_5 from weight of $P_2O_5.24MoO_3$ or $Mg_2P_2O_7$; 0.006, per cent of iron from cc. of $KMnO_4$.

Where a large number of calculations of the same sort must be made, these charts should prove very useful. Their accuracy is sufficient for commercial work, different ranges providing for higher accuracy with low percentages. They have the advantage of showing at a glance the accuracy necessary in weighing the sample or precipitate. In this country it is, however, not customary to weigh the ignited precipitate of phosphomolybdic anhydride.—H. H. WILLARD

Technik der Emulsionen. BY OTTO LANGE. 391 pages. Verlag von Julius Springer, Berlin, 1929. Price, paper, 28 marks; bound, 29.4 marks.

This excellent book on emulsions in the industries should be translated at once into English. Clayton's book on the same subject brought the reader up to 1924 in good style, but Lange's much larger book is essential if the subject is to be brought up to the present year.

Theory is given to some extent in the earlier pages, but the book is essentially industrial, dealing in great detail with emulsifying apparatus and with the relation of emulsions to the mineral oil industry, to soaps, cosmetics, milk, rubber, cellulose, paper, mortar, cements, and many other products.

The sixty-six drawings are very helpful, but an index is lacking.—HARRY N. HOLMES

MARKET REPORT—JULY, 1929

FIRST-HAND PRICES FOR CHEMICALS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET ON JULY 15

Newer Chemicals

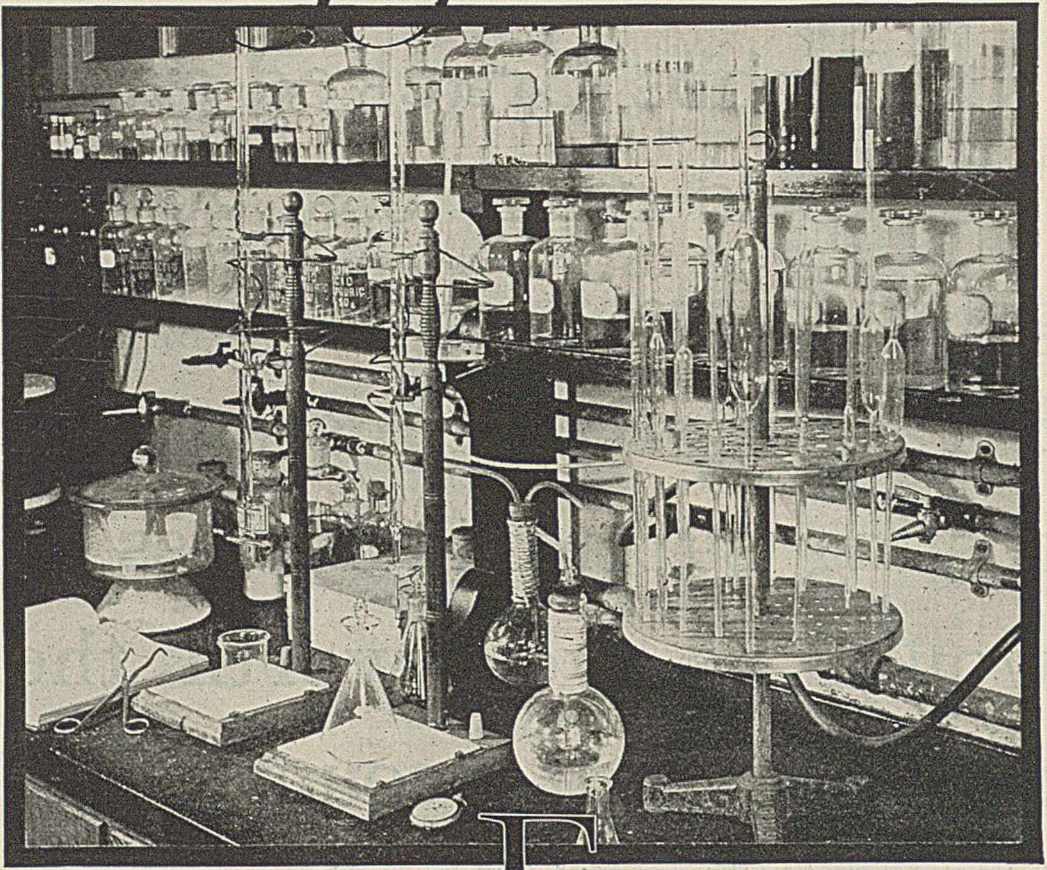
Acetaldehyde, drums, lc-l., wks.	lb.	.18½
Acetaldol, 50-gal. drums	lb.	.27
Acetylene tetrachloride, *see* Tetrachloroethane		
Aldol, c/l., wks.	lb.	.27
Amyl furoate, 1-lb. tins	lb.	5.00
Butyl carbitol, *see* Diethylene glycol monobutyl ether		
Cellosolve, *see* Ethylene glycol monobutyl ether		
Furoate, tech., 50-gal. drums	lb.	.50
Carbitol, *see* Diethylene glycol monomethyl ether		
Cellosolve, *see* Ethylene glycol monoethyl ether		
Acetate, *see* Ethylene glycol monoethyl ether acetate		
Cellulose acetate, 50-lb. kegs	lb.	1.25
Crotonaldehyde, 50-gal. drums	lb.	.32
Dichloroethylether, 50-gal. drums	lb.	.05
Diethylene glycol, drums	lb.	.10
Monobutyl ether, drums	lb.	.28
Monoethyl ether, drums	lb.	.13
Monomethyl ether, 50-gal. drums, c/l	lb.	.15
Diethylene oxide, 50-gal. drums	lb.	
Dioxan, *see* Diethylene oxide		
Diphenyl, c/l.	lb.	.40
Ethyl acetoacetate, 50-gal. drums	gal.	.65
Carbonate, 90%, 50-gal. drums	gal.	1.85
Chlorocarbonate, 50-gal. drums	gal.	.35
Ether, absolute, 50-gal. drums	lb.	.50
Furoate, 1-lb. tins	lb.	5.00
Ethylene chlorhydrin, 40-, 50-, 90-gal. drums	lb.	.75
Dichloride, 50-gal. drums	lb.	.05
Glycol, 50-gal. drums	lb.	.25
Monobutyl ether, drums, wks.	lb.	.24
Monoethyl ether, drums, wks.	lb.	.17
Monoethyl ether acetate, drums, wks.	lb.	.20
Monomethyl ether, drums	lb.	.20
Oxide, cyl.	lb.	2.00
Furfuramide (tech.), 100-lb. drums	lb.	.30
Furfuryl acetate, 1-lb. tins	lb.	5.00
Alcohol, tech., 100-lb. drums	lb.	.50
Furoic acid (tech.), 100-lb. drums	lb.	.50
Helium, 1-liter bot.	liter	25.00
Lead dithiofuroate, 100-lb. drums	lb.	1.00
Magnesium peroxide, 100-lb. cs.	lb.	1.25
Methyl acetate, drums	gal.	.95
Cellosolve, *see* Ethylene glycol monomethyl ether		
Furoate, tech., 50-gal. drums	lb.	.50
Paraldehyde, 110–55 gal. drums	lb.	.20½
Phosphorus oxychloride, 175 cyl.	lb.	.35
Propyl furoate, 1-lb. tins	lb.	5.00
Strontium peroxide, 100-lb. drums	lb.	1.25
Sulfuryl chloride, 600-lb. drums, crude	lb.	.10
Distilled	lb.	.35
Tetrachloroethane, 50-gal drums	lb.	.09
Trichloroethylene, 50-gal. drums	lb.	.10
Triethanolamine, 50-gal. drums	lb.	.55
Vinyl chloride, 16-lb. cyl.	lb.	1.00
Zinc dithiofuroate, 100-lb. drums	lb.	1.00
Perborate, 100-lb. drums	lb.	1.25
Peroxide, 100-lb. drums	lb.	1.25

Chemicals Previously Quoted

Acetanilide, U. S. P., bbls.	lb.	.36
Acetic anhydride, 92–95%, cbys.	lb.	.29
Acetone, C. P., drums, wks.	lb.	.15
Acetophenetidine, bbls.	lb.	1.40
Acid, acetic, 28%, c/l. bbls.	100 lbs.	3.88
56%, c/l. bbls.	100 lbs.	7.35
Glacial, c/l. bbls.	100 lbs.	13.68
Acetylsalicylic, bbls.	lb.	.85
Anthranilic, 99–100%, drums	lb.	.98
Benzoic, tech., bbls.	lb.	.57
Boric, bbls.	lb.	.05¾
Butyric, 60%, pure, 5-lb. bot.	lb.	.55
Chloroacetic, mono-, bbls., wks.	lb.	.21
Di-, cbys.	lb.	1.00
Tri-, bbls.	lb.	2.50
Chlorosulfonic, drums, wks.	lb.	.05
Chromic, pure, 98%, drums	lb.	.21
Cinnamic, 5-lb. cans	lb.	3.25
Citric, U. S. P., kegs, bbls.	lb.	.46
Cresylic, pale, drums	gal.	.72
Formic, 90%, cbys., N. Y.	lb.	.11
Gallic, U. S. P., bbls.	lb.	.74
Glycerophosphoric, 25%, 1-lb. bot.	lb.	1.40
H, bbls., wks.	lb.	.68
Hydriodic, 10%, U. S. P., 5-lb. bot.	lb.	.80
Hydrobromic, 48%, cbys., wks.	lb.	.45
Hydrochloric, 20°, tanks, wks.	100 lbs.	1.10
Hydrofluoric, 30%, bbls., wks.	lb.	.06
60%, bbls., wks.	lb.	.13
Hydrofluosilicic, 35%, bbls., wks.	lb.	.11
Hypophosphorus, 30%, U. S. P., 5-gal. demis	lb.	.85
Lactic, 22%, dark, bbls.	lb.	.04¼
66%, light, bbls., wks.	lb.	.26
Mixed, tanks, wks.	N unit	.07
	S unit	.01
Molybdic, 85%, kegs	lb.	1.25
Naphthionic, tech., bbls.	lb.	nom.
Nitric, C. P., cbys.	lb.	.12
Nitric, 38°, c/l. cbys., wks.	100 lbs.	5.00
Oxalic, bbls., wks.	lb.	.11
Phosphate, bulk	ton	10.00
Phosphoric, 50%, cbys.	lb.	.08
Picramic, bbls.	lb.	.65
Picric, bbls., c/l.	lb.	.40
Pyrogallic, tech., bbls.	lb.	.86
Salicylic, tech., bbls.	lb.	.37
Stearic, d. p., bbls., c/l.	lb.	.15¼
Sulfanilic, 250-lb. bbls.	lb.	.15
Sulfuric, 66°, c/l. cbys., wks.	100 lbs.	1.35
66°, tanks, wks.	ton	15 50
60°, tanks, wks.	ton	11.00
Oleum, 20%, tanks, wks.	ton	18.50
40%, tanks, wks.	ton	42.00
Sulfurous, U. S. P., 6%, cbys.	lb.	.05
Tannic, tech., bbls.	lb.	.35
Tartaric, U. S. P., cryst., bbls.	lb.	.38
Tungstic, kegs	lb.	2.00
Valeric, C. P., 10-lb. bot.	lb.	2.50
Alcohol, U. S. P., 190 proof, bbls.	gal.	2.69½
Amyl, 10%, Imp. drums	gal.	1.75
Butyl, drums, c/l., wks.	lb.	.17¾
Cologne spirit, bbls.	gal.	2.69
Denatured. No. 5, comp. denat., c/l. drums	gal.	.50
No. 1. comp. denat., drums	gal.	.51
Isoamyl, drums	gal.	3.50
Isobutyl, ref., drums	lb.	1.00
Isopropyl, ref., drums	gal.	1.25
Propyl, ref., drums	lb.	1.00
Wood, *see* Methanol		
Alpha-naphthol, bbls.	lb.	.65
Alpha-naphthylamine, bbls.	lb.	.32
Alum, ammonia, lump, bbls., wks.	100 lbs.	3.25
Chrome, casks, wks.	100 lbs.	5.25
Potash, lump, bbls., wks.	100 lbs.	3.00
Soda, bbls., wks.	100 lbs.	3.75
Aluminum, metal, N. Y.	lb.	.240
Aluminum chloride, anhyd., drums	lb.	.05
Aluminum stearate, 100-lb. bbl.	lb.	.25
Aluminum sulfate, comm'l, bags, wks.	100 lbs.	1.40
Iron-free, bags, wks.	100 lbs.	1.95
Aminoazobenzene, 100-lb. kegs	lb.	1.15
Ammonia, anhydrous, cyl., wks.	lb.	.14
Ammonia water, 26°, drums, wks.	lb.	.03¼
Ammonium acetate, kegs	lb.	.34
Bifluoride, bbls.	lb.	.21
Bromide, 50-lb. boxes	lb.	.48
Carbonate, tech., casks	lb.	.09
Chloride, gray, bbls.	100 lbs.	5.40
Lump, casks	lb.	.11
Iodide, 25-lb. jars	lb.	5.20
Nitrate, tech., cryst., bbls.	lb.	.06
Oxalate, kegs	lb.	.35
Persulfate, cases	lb.	.31
Phosphate, dibasic, tech., bbls.	lb.	.13
Sulfate, bulk, wks.	100 lbs.	2.05
Thiocyanate, tech., kegs	lb.	.40
Amyl acetate, tech., drums	gal.	1.65
Aniline oil, drums	lb.	.15¼
Anthracene, 80–85%, casks, wks.	lb.	.60
Anthraquinone, subl., bbls.	lb.	.85
Antimony, metal	lb.	.08⅞
Antimony chloride, anhyd., drums	lb.	.17
Oxide, bbls.	lb.	.09¼
Salt, dom., bbls.	lb.	.26
Sulfide, crimson, bbls.	lb.	.25
Golden, bbls.	lb.	.16
Vermilion, bbls.	lb.	.38
Tartrolactate, bbls.	lb.	.45
Argols, red powder, bbls.	lb.	.08
Arsenic, metal, kegs	lb.	.50
Red, kegs, cases	lb.	.09
White, c/l. kegs	lb.	.03¾
Asbestine, bulk, c/l.	ton	15.00
Barium carbonate, bbls., bags, wks.	ton	58.00
Chloride, bags, wks.	ton	65.00
Dioxide, bbls., wks.	lb.	.12
Hydroxide, bbls.	lb.	.04¾
Nitrate, casks	lb.	.08¼
Barium sulfocyanate, 400-lb. bbls.	lb.	.27
Barytes, floated, 350-lb. bbls., wks.	ton	23.00
Benzaldehyde, tech., drums	lb.	.65
F. F. C., cbys.	lb.	1.40
U. S. P., cbys.	lb.	1.15
Benzene, pure, tanks, mills	gal.	.23
Benzidine base, bbls.	lb.	.70
Benzoyl chloride, cbys.	lb.	1.00
Benzyl acetate, cbys.	lb.	1.30
Alcohol, 5-liter bot.	lb.	1.40
Chloride, tech., drums	lb.	.30
Beta-naphthol, bbls.	lb.	.24
Beta-naphthylamine, bbls.	lb.	.63
Bismuth, metal, cases	lb.	1.70
Bismuth, nitrate, 25-lb. jars	lb.	1.80
Oxychloride, boxes	lb.	3.10
Subnitrate, U. S. P., 25-lb. jars	lb.	1.60
Blanc fixe, dry, bbls.	ton	80.00
Bleaching powder, drums, wks.	100 lbs.	2.25
Bone ash, kegs	lb.	.06
Bone black, bbls.	lb.	.08¼
Borax, bags	lb.	.02½
Bordeaux mixture, bbls.	lb.	.10½
British gum, com., c/l.	100 lbs.	4.37
Bromine, bot.	lb.	.45
Bromobenzene, drums	lb.	.50
Bromoform, 5-lb. bot.	lb.	1.65
Butylacetate, 100-gal. drums	gal.	1.35
Cadmium bromide, 50-lb. jars	lb.	1.20
Cadmium, metal, boxes	lb.	.65
Cadmium sulfide, cs.	lb.	1.00
Caffeine, U. S. P., 5-lb. cans	lb.	2.90
Calcium acetate, bags	100 lbs.	4.50
Arsenate, bbls.	lb.	.07
Carbide, drums	lb.	.05
Chloride, drums, wks.	ton	20.00
Cyanide, 100-lb. drums	lb.	.30
Lactate, tech., bbls.	lb.	.35

Nitrate, bbls	ton	52.00
Phosphate, monobas., bbls	lb.	.08
Tribas., bbls	lb.	.11
Calcium carbonate, tech., bgs.	100 lbs.	1.00
U. S. P., precip., 175-lb. bbl	lb.	.06½
Camphor, Jap., cases	lb.	.60
Camphor, monobrom, cs	lb.	1.85
Caramel, bbls	gal.	.63
Carbazole, bbls	lb.	.15
Carbon, activated, drums	lb.	.10
Carbon bisulfide, drums	lb.	.05½
Carbon black, cases	lb.	.12
Carbon dioxide, liq., cyl	lb.	.06
Carbon tetrachloride, drums	lb.	.07
Casein, stand. gr., bbls	lb.	.15
Cellulose acetate, kegs	lb.	1.25
Cerium oxalate, kegs	lb.	.32
Charcoal, willow, powd., bbls	lb.	.06
China clay, imp., bags	100 lbs.	15.00
Chloral hydrate, drums	lb.	.60
Chloramine, U. S. P., 5-lb. bot	lb.	1.75
Chlorine, liq., c/l., cyl	lb.	.04½
Chlorobenzene, mono-, drums	lb.	.09
Chloroform, tech., drums	lb.	.16
Chromium acetate, 20° soln., bbls	lb.	.05½
Coal tar, tanks, bbls., wks	gal.	.07
Cobalt, metal, kegs	lb.	2.50
Cobalt oxide, bbls	lb.	2.10
Cod-liver oil, bbls	bbl.	30.00
Collodion, drums	lb.	.23
Copperas, c/l., bulk	ton	13.00
Copper, metal, elec	100 lbs.	17.78
Copper carbonate, bbls	lb.	.19
Chloride, bbls	lb.	.25
Cyanide, drums	lb.	.55
Oxide, red, bbls	lb.	.25
Sulfate, c/l., bbls	100 lbs.	6.00
Cotton, soluble, bbls	lb.	.40
Cream tartar, bbls	lb.	.26½
Cyanamide, bulk, N. Y.	Ammon. unit	1.70
Diaminophenol, kegs	lb.	3.80
Dianisidine, kegs	lb.	3.00
Dibutylphthalate, drums, wks	lb.	.26
Diethylaniline, drums	lb.	.55
Diethylene glycol, l. c. l. lots, drums	lb.	.12
Carload lots, drums	lb.	.10
Diethyl phthalate, drums	lb.	.24
Diethyl sulfate, tech., drums	lb.	.30
Dimethylaniline, drums	lb.	.30
Dimethylsulfate, drums	lb.	.45
Dinitrobenzene, drums	lb.	.15½
Dinitrochlorobenzene, bbls	lb.	.15
Dinitronaphthalene, bbls	lb.	.35
Dinitrophenol, bbls	lb.	.31
Diphenylamine, bbls	lb.	.40
Diphenylguanidine, bbls	lb.	.36
Epsom salt, tech., bbls., c/l., N. Y.	100 lbs.	1.70
Ether, nitrous, bot	lb.	.80
Ether, U. S. P., drums	lb.	.38
Ethyl acetate, 85%, drums	gal.	.95
Bromide, drums	lb.	.55
Chloride, drums	lb.	.22
Methyl ketone, drums	lb.	.30
Ethylbenzylaniline, 300-lb. drums	lb.	1.05
Ethylene dichloride, tanks	lb.	.05
Chlorohydrin, anhyd., drums	lb.	.75
Glycol, c/l., wks	lb.	.25
Feldspar, bulk	ton	20.00
Ferric chloride, tech., bbls	lb.	.07½
Ferrous chloride, cryst., bbls	lb.	.06
Ferrous sulfide, bbls	100 lbs.	2.50
Fluorspar, 98%, bags	ton	41.00
Formaldehyde, bbls	lb.	.09½
Formaniline, drums	lb.	.38
Fuller's earth, bags, c/l., mines	ton	15.00
Furfural, 500-lb. drums., c/l	lb.	.17½
Glauber's salt, bbls	100 lbs.	1.10
Glucose, 70°, bags, dry	100 lbs.	3.14
Glycerol, C. P., drums	lb.	.15
G salt, bbls	lb.	.50
Hexamethylenetetramine, tech., drums	lb.	.50
Hydrogen peroxide, 25 vol., bbls	lb.	.06½
Hydroquinone, kegs	lb.	1.25
Indigo, 20%, paste, bbls	lb.	.15
Iodine, crude, 200-lb. kgs	lb.	4.20
Iodine, resubl., jars	lb.	4.65
Iodoform, bot	lb.	6.00
Iridium, metal	oz.	280.00
Kieselguhr, bags	ton	60.00
Lead, metal	100 lbs.	6.70
Lead acetate, bbls., white	lb.	.13
Arsenate, bbls	lb.	.13
Oxide, litharge, bbls	lb.	.08¾
Peroxide, drums	lb.	.25
Red, bbls	lb.	.09½
Sulfate, bbls	lb.	.08¼
White, basic carb., bbls	lb.	.09
Lime, hydrated, bbls	100 lbs.	.85
Lime, live, chemical, bbls., wks.	100 lbs.	1.05
Limestone, ground, bags, wks	ton	4.50
Lithium carbonate, 100-lb. kgs	lb.	1.45
Lithopone, bbls	lb.	.05¾
Magnesite, crude	ton	36.00
Calcined, 500-lb. bbls., wks	ton	50.00
Magnesium, metal sticks, wks	lb.	.85
Magnesium carbonate, bags	lb.	.06
Chloride, drums	ton	36.00
Fluosilicate, cryst., bbls	lb.	.10
Oxide, U. S. P., light, bbls	lb.	.42
Manganese chloride, casks	lb.	.08
Dioxide, 80%, bbls	ton	80.00
Sulfate, casks	lb.	.08
Mercury bichloride, cryst., 25 lbs	lb.	1.66
Mercury, flasks, 75 lbs	flask	123.00
Meta-nitroaniline, bbls	lb.	.72
Meta-phenylenediamine, bbls	lb.	.84
Meta-toluylenediamine, bbls	lb.	.70
Methanol, pure, drums	gal.	.67
Denaturing grade, tanks	gal.	.60
Methyl acetone, drums	gal.	.83
Salicylate, cases	lb.	.42
Methyl chloride, cylinders	lb.	.55
Michler's ketone, bbls	lb.	3.00
Monoethylaniline, drums	lb.	1.05
Naphtha, solvent, tanks	gal.	.35
Naphthalene, flake, bbls	lb.	.05
Nickel, metal	lb.	.35
Nickel salt, single, bbls	lb.	.13
Double, bbls	lb.	.13
Niter cake, bulk	ton	16.00
Nitrobenzene, drums	lb.	.10¼
Oil, castor, No. 1	lb.	.13
China wood, bbls	lb.	.14¾
Coconut, Ceylon, tanks	lb.	.08⅜
Cod, N. F., tanks	gal.	.60
Corn, crude, tanks, mills	lb.	.07⅞
Cottonseed, crude, tanks	lb.	nom.
Lard, edible, bbls	lb.	.15
Linseed, bbls	lb.	.105
Menhaden, crude, tanks	gal.	.52
Neat's-foot, pure, bbls	lb.	.13½
Oleo, No. 1, bbls	lb.	.10¾
Olive oil, denat., bbls	gal.	1.35
Foots, bbls	lb.	.10
Palm, Lagos, casks	lb.	.07½
Peanut, crude, bbls	lb.	nom.
Perilla, bbls	lb.	.15½
Rapeseed, bbls., English	gal.	.85
Red, bbls	lb.	.10⅜
Soy bean, crude, bbls	lb.	.11½
Sperm, 38°, bbls	gal.	.84
Whale, bbls., natural, winter	gal.	.78
Ortho-aminophenol, kegs	lb.	2.20
Ortho-anisidine, drums	lb.	2.50
Ortho-dichlorobenzene, drums	lb.	.08
Ortho-nitrochlorobenzene, drums	lb.	.32
Ortho-nitrophenol, bbls	lb.	.85
Ortho-nitrotoluene, drums	lb.	.17
Ortho-toluidine, bbls	lb.	.27
Palladium, metal	oz.	46.80
Para-aminophenol, kegs	lb.	1.02
Para-dichlorobenzene	lb.	.17
Para-formaldehyde, cases	lb.	.40
Paraldehyde, tech., drums	lb.	.23
Para-nitroaniline, drums	lb.	.48
Para-nitrochlorobenzene, drums	lb.	.25
Para-nitrophenol, bbls	lb.	.50
Para-nitrosodimethylaniline, bbls.	lb.	.92
Para-nitrotoluene, bbls	lb.	.30
Para-phenylenediamine, bbls	lb.	1.15
Para-toluidine, bbls	lb.	.40
Paris Green, 250-lb. kegs	lb.	.25
Phenol, drums	lb.	.13¼
Phenolphthalein, drums	lb.	1.10
Phenylethyl alcohol, 1-lb. bot	lb.	7.00
Phosphorus, red, cases	lb.	.60
Phosphorus trichloride, cyl	lb.	.35
Phthalic anhydride, bbls	lb.	.18
Platinum, metal	oz.	68.00
Potash, caustic, drums	lb.	.07⅛
Potassium acetate, kegs	lb.	.29
Bicarbonate, casks	lb.	.13
Bichromate, casks	lb.	.09¼
Binoxalate, bbls	lb.	.16
Bromate, cs	lb.	.35
Carbonate, 80–85%, calc., casks	lb.	.05¾
Chlorate, kegs	lb.	.08½
Chloride	ton	34.55
Cyanide, cases	lb.	.55
Meta-bisulfite, bbls	lb.	.12
Permanganate, drums	lb.	.16
Prussiate, red, casks	lb.	.39
Yellow, casks	lb.	.18½
Titanium oxalate, bbls	lb.	.21
Pyridine, drums	gal.	1.75
Quinine bisulfate, 100 oz	oz.	.40
Sulfate, 100-oz. cans	oz.	.40
Resorcinol, tech., kegs	lb.	1.20
Rochelle salt, bbls., U. S. P	lb.	.23
R salt, bbls	lb.	.45
Saccharin, cans	lb.	1.75
Salt cake, bulk	ton	19.00
Saltpeter, gran., bbls	lb.	.06⅛
Silica, ref., bags	ton	22.00
Silver nitrate, 16-oz. bot	oz.	.40¼
Soda ash, 58%, light, bags, contract, wks	100 lbs.	1.32
Soda, caustic, 76%, solid, drums, contract, wks	100 lbs.	2.90
Sodium acetate, bbls	lb.	.05¾
Benzoate, bbls	lb.	.50
Bicarbonate, bbls	100 lbs.	2.41
Bichromate, casks	lb.	.07½
Bisulfite, bbls	lb.	.04
Bromide, bbls	lb.	.42
Carbonate, sal soda, bbls	100 lbs.	1.30
Chlorate, kegs	lb.	.09
Chloride, bags	ton	12.00
Cyanide, cases	lb.	.18
Fluoride, bbls	lb.	.09
Metallic, drums, 12¼-lb. bricks	lb.	.27
Naphthionate, bbls	lb.	.55
Nitrate, crude, bags, N. Y.	100 lbs.	2.10
Nitrite, bbls	lb.	.08
Perborate, bbls	lb.	.20
Peroxide, cases	lb.	.27
Phosphate, trisodium	lb.	.04
Picramate, kegs	lb.	.69
Prussiate, bbls	lb.	.12
Silicate, drums, tanks, 40°	100 lbs.	1.65
Silicofluoride, bbls	lb.	.05¼
Stannate, drums	lb.	.41½
Sulfate, anhyd., bbls	lb.	.02½
Sulfide, cryst., bbls	lb.	.02½
Solid, 60%	lb.	.03½
Sulfocyanide, bbls	lb.	.40
Thiosulfate, reg., cryst., bbls	lb.	.02½
Tungstate, kegs	lb.	1.40
Strontium carbonate, bbls	lb.	.07¼
Nitrate, bbls	lb.	.09
Strychnine alkaloid, 100 oz., powder	oz.	.56
Sulfate, powder	oz.	.46
Sulfur, bulk, mines, wks	ton	18.00
Sulfur chloride, red, drums	lb.	.05
Yellow, drums	lb.	.03½
Sulfur dioxide, commercial, cyl	lb.	.08
Sulfuryl chloride, drums	lb.	.10
Thiocarbanilid, bbls	lb.	.22
Tin, Amer., stand	lb.	.45⅛
Tin bichloride, 50% sol., bbls	lb.	.14½
Oxide, bbls	lb.	.50
Titanium oxide, bbls., wks	lb.	.24
Toluene, tanks	gal.	.40
Tribromophenol, cases	lb.	1.10
Triphenylguanidine, drums	lb.	.60
Triphenyl phosphate, bbls	lb.	.70
Tungsten	WO_3 unit	15.50
Urea, pure, cases	lb.	.25
Whiting, bags	ton	18.00
Xylene, 5°, drums, mills	gal.	.40
Xylidine, drums	lb.	.38
Zinc, metal, N. Y	100 lbs.	7.05
Zinc ammonium chloride, bbls	lb.	.05⅛
Chloride, granulated, drums	lb.	.06¼
Oxide, Amer., bbls	lb.	.07⅜
Stearate, bbls	lb.	.25
Zinc dust, bbls., kegs, c/l	lb.	.08½

Out of 33,000 compounds



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