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The Editor's Point of View

TRUTH WILL PREVAIL. This old saying is undoubtedly true, but it frequently happens that it is almost impossible to bring the truth clearly into the open, and where technicalities are concerned to present even proved facts in such a fashion that those who run may not only read but be able to discriminate and comprehend.

A syndicated anonymous article circulated widely under the auspices of the *American Weekly, Inc.*, was distributed January 3 and devoted a page to the "Next War." This is a fanciful, misleading, and false statement, in which the style is quite unhampered by any regard for such trivial things as facts established and the truth. The page is composed largely of illustrations, which for the most part are mere figments of imagination. Heretofore those who are not interested in any defense of the country and who have centered their efforts upon chemical reagents, because they are least understood by the general public, have based their arguments on what might happen in unprotected areas and among civilians. In this tale an effort is made to increase the tempo by printing an imaginative picture, entitled "Rescue brigade searching the parks to find nurses who have been overcome and the babies suffocated in their baby carriages."

Of course the article is anonymous. This kind usually is. And the author, undoubtedly far from proud of his work performed for a few dollars, remains carefully hidden by the editors using this material, although the publication of such rot casts serious reflection upon the intelligence of these same editors. Efforts to present exact knowledge through like channels fail, and those who have lately led the continuous organized and generously supported attacks on the chemistry of war steadfastly decline to expose themselves to the truth. They decline to receive those who come in a friendly spirit for the sole purpose of talking the thing out and offering a few authenticated facts.

As in all articles of this sort, exaggeration, gross unfamiliarity with chemistry, and imaginative statements make up the story. The idea that defenseless civilians in cities offer the greatest target for chemicals is of course erroneous. Cities and the materials of war which they supply to troops are unquestionably destroyed with more efficiency and lower cost by high explosives, whether dropped from aircraft or shot from long distances. The roof area of a city is greater than that of its streets, and gas sprayed according to the article would fall on roofs, where it would remain to evaporate in the air or be washed off by rain, or upon the streets, from which it could be quickly hosed by any fire department. The population on the upper floors of houses and in apartment buildings with doors and windows closed would find themselves well protected. It is not so easy to destroy gas in the open field as it is upon city streets and roofs, and aside from a possible psychological advantage nothing appears to be gained by wasting expensive chemicals and risking aircraft over protected cities. High explosives are better for such work.

Mustard gas, which from many points of view was the most effective, is always given exaggerated potentialities in newspaper chemistry. The facts are that, during the last war, it took two tons of mustard gas to produce one death and one ton of mustard to produce twenty-nine casualties. These figures are based on the combined data of all the nations engaged in the war. Why will not those who center their argument on chemical warfare make a similar comparison with the machine gun? We are told that a ton of mustard would destroy the whole city of New York. That could be possible only if as much as 20 milligrams of the compound were injected into the lungs of each individual. Now consider the machine gun. A machine gun bullet would kill 3 men if they were standing back to chest. A machine gun can fire 600 bullets a minute, and therefore could kill 1800 such men per minute. A few machine guns in 24 hours could wipe out the population of New York City, providing of course the citizens were obliging enough to march by in rows. The destruction of the population by mustard gas is just as fanciful.

The article to which we take exception, while overestimating the destructiveness of gas, goes far to underestimate the efficiency of the gas mask. While it is true that the mask developed during the war was not proof against irritant smoke, at the present time our Army gas mask is equipped with a canister which affords protection, not only against smokes, but against every other type of chemical agent which so far has been conceived as at all useful in warfare. It is not necessary to have a special type of canister for use against each of the various chemicals, as the anonymous author alleges. The statement that "all countries are working on a tear gas that will penetrate the mask as mustard gas penetrates clothing" is probably far from the truth, for based on our present knowledge of chemicals it does not appear at all possible that such a gas can be contrived. Chemists cannot help but smile at the statement that "now all countries are working on gases intended to make junk out of every firearm from the officer's pistol to the heaviest cannon and every engine from motor truck to tank. These gases, destructive to metals but harmless to men, may be used against munition factories, ordnance plants, motor factories, and other places where war machinery is concentrated but not in the cities where wholesale slaughter is the plan." Newspaper chemistry, indeed! We know that some of the materials that have been used in war are highly corrosive, but it has taken this writer to raise the destructiveness of these chemicals to the *n*th degree by just a few punches of the typewriter keys.

And listen to this! "The United States Chemical Warfare Service is hard at work to offset another sort of humane gas which attacks soldiers' uniforms, causing them to fall off in shreds. Future battles may be fought by naked soldiers. In that case officers' insignia may have to be tattooed on their arms."

As if that were not enough to please the fancy, the author then pictures a new kind of gas to be used by ships. "A fleeing fleet heading into the wind could pour from its sterns tons of chemicals which combining with the salt water would make the ocean behind them unbreathable for miles." But wait, all the advantage is not to be with the fleet. "The planes of the pursuing fleet would fly ahead and drop the same medicine for the fugitives." Unfortunately, we are left to wonder who comes out ahead in this newspaper warfare. Again, "Merchant ships will run afoul of these gas mines too and may go steaming on with every one on board dead." The author's lack of chemical sense is demonstrated by reference to the use of hydrocyanic gas. It was proved in the great war that its physical characteristics unsuit it for such use.

But the saddest part of all is in the last paragraph. "As women congregate in cities and except for comparatively few nurses do not get near the front, the next war may end with a surplus of young men who will come home from the battle field to find a sad scarcity of girls to marry—just the reverse of wars in the past."

It is a pity that it seems necessary to devote valuable space to a discussion of this inanity. But when the lay press lends itself to such propaganda it becomes necessary for the chemists themselves, who are in a position to know, to learn what is transpiring and be prepared to answer sincere questions in a constructive, straightforward, and convincing manner. Those who are responsible for the chemistry of war as applied to our national defense seek opportunities to lay the truth before the people. More than one group which, because of a misunderstanding, might have been prepared to take at face value such an article as we are discussing has acquired an enlightened point of view upon learning the truth.

Chemists, as we have continually stressed, are primarily interested in constructive humanitarian work. They believe it to be just as easy to outlaw and do away with all war as really to do away with the form of defense or offense that is the most humane and effective and the least expensive. The United States, without thinking of offense, must acquire all types of information vital in case of an emergency. Nothing is more important than chemistry as it may be applied in any and all forms of effective defense. Any other point of view is not only unsafe but in the last analysis dangerously un-American. Let the truth be known—it will prevail.

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EVERY TUB ON ITS OWN BOTTOM. In discussing the rapid advance made in his own field, a director of a prominent company recently said to us that he found it difficult to make any sort of reasonable return on research investment before some new thing had to be taken up, often displacing its immediate predecessor. We cannot stop progress, so it behooves us to find some way of preventing the waste which might easily result from too great speed.

The plant that insists upon spreading out research and development costs over a long period of years may have the advantage of lower initial selling prices, but it also runs the risk of obsolescence overtaking it before it finds itself ready to make desirable readjustments. The company that writes off original costs out of profits and rapidly prepares itself to come to the end of each separate enterprise undoubtedly follows the wise course. Such a policy is based on the realization that, no matter how good a product may be, it is not reasonable to assume that it will long remain the best in its field. Each new thing must not only pay its way after commercialization, but it should also pay for its research and development. Under such a method special buildings and equipment are soon written off and the management is found ready for the next progressive step.

While such a system may lead to a somewhat higher price for new products, experience has shown that consumers can be persuaded of the wisdom of the procedure. The manufacturer who, by means of such a plan, is always ready to undertake new improvements for the sake of his trade is in position to render service that is of value to his customers and which cannot be offered by the concern that is handicapped by a less forward-looking method. Every modern business should endeavor so to shape its policy that, when the time comes to drop some article, no matter how new it may be, in favor of a still better one, there will be no difficulty in immediately making the change.

There are many instances where whole industries have failed to follow this procedure. Some not only have been handicapped but individual plants have liquidated and closed up shop. The picture is very different in those cases where every tub has been placed on its own bottom and where there is elasticity ready to accommodate each new changing order.

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CAPITALIZING OUR DIFFICULTIES. But for the distressing effects upon a considerable number of individuals, it could be shown that the depressing experiences which overtook us in 1929 may be turned into decided benefit. Sober-minded people realize that the general public went on something of a spree from which the recovery is slow and painful. Once recovered, we should have learned enough lessons eventually to make the experience helpful.

Economists tell us that the very elements which caused the high-flying years of 1922 to 1929 were the kind that of themselves prevented that prosperity from being enduring. Much of our export business was sustained by means of loans to foreign countries and individuals abroad, and these can only be repaid against our tariff and in competition with our own production. Increased output per man here did not bring down retail prices and the resulting profits went largely to dividends and to surplus, with labor's share substantially unchanged. The result was an overproduction and an increase in plant which soon surpassed that of the consumer's income to absorb. Increase in bank loans came to depend upon an advance in the prices of securities. Energy was diverted to the production of luxuries for those who were but temporarily able to consume them, and our whole credit structure rested upon stock market prices. More than this, the normal ways by which international trade has been accustomed to adjust itself were blocked. Tariffs and cartels prevented the natural redistribution of gold. War debts and indemnities added their problems to the complex, and money which would normally have gone into purchases was largely used to pay off indebtedness where funds had been borrowed on high-priced securities, to save which payments were necessary in the face of declining bond and stock prices.

The economist suggests a number of ways out. Indeed, the plans to be followed are limited only by the number of those putting them forward. Some say that a creditor nation, such as we have become, must either operate on a low tariff or the tariff may be maintained and production reduced to the requirements of the domestic market. The advocates of the latter procedure point out that, however important export may be to some lines of industry, in general it still represents but a small percentage of our manufactures. Others maintain that reduction of tariffs could do but little harm under present circumstances and that, if all nations should follow that policy, the improved world conditions through reciprocal tariff arrangements would soon counterbalance any small losses.

Other alternatives involve again extending loans, a reduction in capital accounts which would be generally resisted, and the reinflation of prices which is another way of saying that the basis of credit should be greatly broadened. There is one point upon which we think an agreement will be found—that credit, so essential in modern merchandizing, depends on confidence, and confidence in turn rests upon ability to make a profit. How shall profits be made under the conditions which confront us? There is much talk of reducing wages, and this has already been done in some industries where salaries are even more affected. In the past recoveries from business recessions have been followed by such wage cutting, but surely this is the last thing that should be done. The experience of some manufacturers has shown other methods of accomplishing this result.

We visited a plant not long ago where, in the period from September 1, 1929 to September 1, 1930, there had been a decline of 30 per cent in the volume of production. By eliminating frills, all getting to work, and by improved technology with the application of science, it was enabled to make such reductions in wages and salaries per hundred pounds of product as to show an increase in net profit. This was done without reducing the income of the workers. In fact, the management decided the minimum which it felt a man with a small family should have, and where such men were earning less their hours of labor were increased, that their pay envelopes might at least contain this minimum. It was purely a piece of improved management and better technology. In the like period ending September 1, 1931, another 10 per cent in volume of production had been lost, but further changes in the plant have still left a margin of profit on operations. We should add that this plant was by no means inefficient prior to these experiences.

The example we cite may be an individual case, but it cannot be the only organization amenable to such improvement. The application of science is useful during booms, it is indispensable when times are normal, and vital when they become hard.

We hope those qualified will continue their study and analysis of our difficulties. We must devise means to prevent a repetition. The part that science can play and is playing is worthy of emphasis.

RESEARCH MANAGEMENT. For years a consistent and well-sustained effort has been made to acquaint industry with the benefits of research. The subject has been discussed in public and private, with the captains of industry, and the members of their organizations. Sometimes the initiative to do something has originated at the top and been handed down as a program approved for immediate action. In other instances the movement has come from below, commencing perhaps when some workman has found himself unable to do just what was required without additional information which some one had to get. The encouraging results which have met efforts to inform the public have also been a factor, and here and there a power in the world of finance has finally recognized the potentialities of research.

There are those who feel that science has been oversold, and they point to the occasional example of a plant where research has been installed, only to be allowed to languish and die without any material benefit to the organization. Has the layman come to expect too much of science as a result of what he has been told? If so, the fault lies in the telling. Where the former occurs, it is largely due to a neglect of some of the fundamental principles in management.

Research management in its broadest sense goes far beyond planning, for management or control is not a synonym, as many seem to think. It is but a stage, perhaps the first element of laboratory management. Planning leads to scheduling, and this must then be followed by mechanisms that put the plan into effect under control. Ideally, research management brings to bear all possible information relating to what is to be done, how it is to be done, and where it is to be done. It must then determine when the program is to go forward and continue to control this performance. Research management involves not only these principles but proper coördination with other plant activities, a selection and training of research personnel and, if the utmost is to be gained from the effort, includes some well thought out and carefully followed procedure for introducing into plant practice the proved results of research.

The great swing toward industrial research and control is evidenced by the large increase in industrial laboratories, by new facilities for training and instruction in our seats of learning, and by the added number of capable men who have been attracted to science as a career. All this has been covered from time to time in what has been published, but research management has been given but casual discussion in the columns of the technical press.

In January we presented the views of well-known directors of research on the scope and principles of research management and the logical divisions of a research organization. We now present another group of papers continuing the discussion. These are centered on the coördination of laboratory and plant effort, the preparatory and the investigational stages of research, and the functions of a laboratory organization. Subsequent papers will deal with economic features, such as cost accounting, and with the selection of personnel. Attention to these articles will prove profitable and thought-provoking and may lead to the adoption of better procedures in the management of an activity that has become fixed in American industry.

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CHEMICAL ENGINEERING AS A CAREER. Studies yielding data to guide the young man in the choice of a career are of unquestioned importance. During 1931 it was our privilege to print a discussion on the relation between engineering education and income, which was applicable to engineering in general. In this issue a paper by A. H. White discusses more particularly the progress which graduates in chemical engineering make, the kind of work many of them do, and something of their incomes.

In compiling data of this sort the investigator finds difficulty in classifying the men. Obviously, if we could agree upon a definition of an executive it would be possible to add to the figures Professor White gives us those from the experience of our number who have become executives. This would result in another class of highly paid men, with immediate benefit to the average figure. One definition of an executive would seem to restrict that term to those general officers of corporations who hold the rank of manager or higher. Studies made by a nationally recognized board afford a contrast, since in its lists draftsmen, foremen, inspectors, and salesmen are included as executives.

In view of the uncertainties in the study printed herewith, it seemed best to the author to leave executives out of consideration. This doubtless gives a truer picture of what the average graduate in chemical engineering may expect to attain.

The advantages of thorough training, preferably carried through to the doctor's degree, stand out rather clearly. This is not surprising, and in fact in these later years has been pretty generally recognized as true. Formerly those who employed such men were slow to appreciate the value of thorough preliminary training. Even now in some quarters there is a tendency to choose some inexperienced young man and train him in the way he should go, rather than take the one who has continued his studies, thereby gaining in many forms of experience. He comes to his employer better fitted to accommodate himself to particular requirements, analyze problems peculiar to the industry with which he is associated, and more able to proceed toward a definite goal without great supervision.

The discussions to which we have referred speak well for the profession, and the data compiled should be of real assistance to students and their advisers.

The Handling of Corrosive Gases

THOMAS H. CHILTON AND WILLIAM R. HUEY
E. I. du Pont de Nemours & Co., Wilmington, Del.

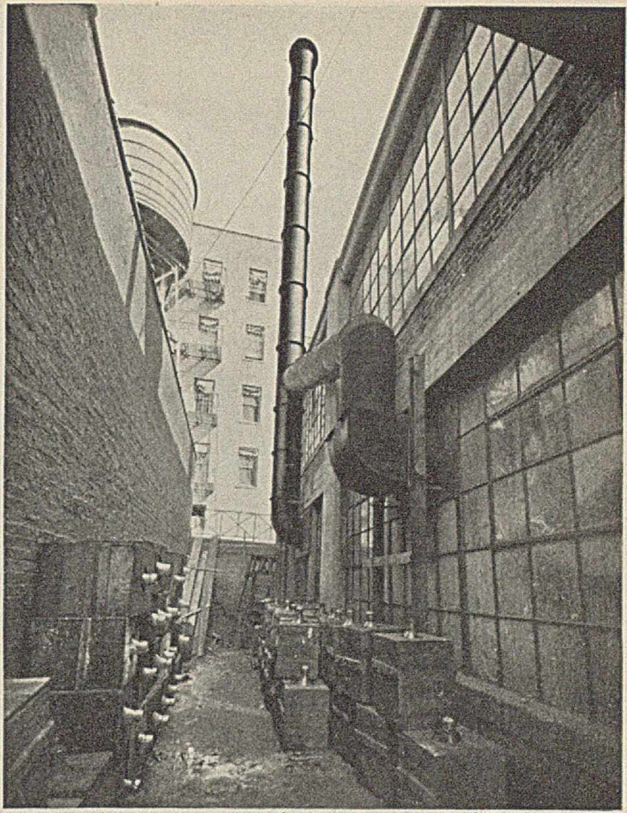
Gases are corrosive at ordinary temperatures only in the presence of moisture. Resistance to moist gaseous corrosive agents can be obtained in the same way as resistance to the same agents when dissolved in water, and available materials and methods for the common cases are listed.

Direct gaseous attack at high temperatures is of two types: surface compound formation, and disintegration. Some principles can be laid down for resistance to surface attack. Metals for resistance to high-temperature attack are listed from several sources.

THE mention of corrosive gases brings to the chemist's mind the thought of oxides of nitrogen, hydrochloric acid vapors, and sulfurous fumes. A moment's reflection, however, will recall to him that these gases are not intrinsically corrosive, for it is well known that liquid sulfur dioxide is safely handled in iron cylinders, and even liquefied nitrogen peroxide has been stored the same way. What then is gaseous corrosion? Or, when are gases corrosive? The present article will attempt to supply some answers to the second question and to outline some of the methods available for meeting the challenge of corrosive gases.

TYPES OF GASEOUS CORROSION

There are at least two distinct types of action by gases on metals. The first is corrosion in the more commonly accepted sense of the word, which is seldom if ever exhibited by single pure gases. This type is exemplified by the action of moist atmospheres containing corrosive agents, such as hydrochloric acid vapor. Here the action is electrochemical in nature and is, in general, similar to that of the same agent when dissolved in water. The second is a direct combination of the gas with the metal, as the formation of oxide scale on iron when heated in air. A third type may be distinguished from the second in that there is no apparent surface change, yet the structure of the metal is altered, possibly by attack of the minor essential ingredients. The embrittlement of steel by hydrogen at high temperatures is an example. The answer to the question, When are gases corrosive?, can be approached by a consideration of these different actions of gases on metals:



Courtesy American Hard Rubber Co.

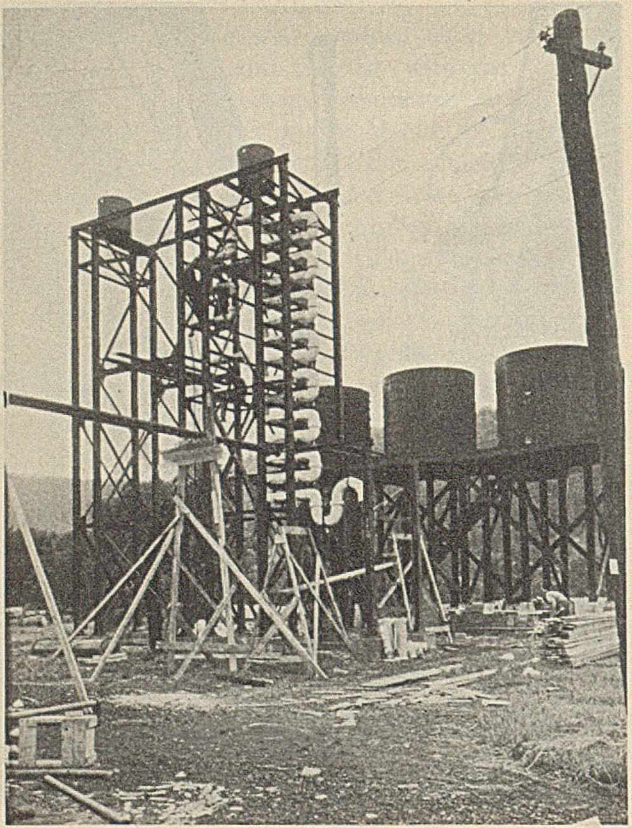
FIFTY-TWO FOOT STACK LINED WITH "ACE" HARD RUBBER

Carries off acid fumes and assures perfect ventilation in modern etching plant

1. Electrochemical attack, dependent on the presence of a conducting film.
2. Direct gaseous attack: (*a*) surface attack, and (*b*) disintegration.

There has been a growing appreciation of the necessity for the presence of a conducting film on the surface of the metal in the first type of corrosion by gaseous agents. It is not necessary at this date to review the electrochemical theory of corrosion by liquids. It should be sufficient to state that all of the principles involved in it are applicable to corrosion by gases, under such conditions that an electrolyte is present on the surface. The only important distinctions are, that with gas mixtures containing oxygen there is everywhere a plentiful supply of this element; and the products of corrosion are less likely to be removed, since this would require a higher velocity of a gas than of a liquid reagent.

While atmospheric corrosion, the literature on which has reached enormous proportions, will not be considered specifically here, it is noteworthy that the most informative recent work has approached the problem from the standpoint of the corrosive gases present in the atmosphere and particularly in relation to the moisture content. Vernon (*22*), for example, having previously shown that the corrosion of copper is due to sulfur dioxide, now finds that copper is not attacked appreciably by completely dry air at ordinary temperatures, even in the presence of as much as 10 per cent sulfur dioxide. In the presence of moisture, however, even small concentrations of sulfur dioxide cause a rapid attack. The rate depends on the humidity, and there is a rapid increase in the rate between 63 and 75 per cent relative humidity. He finds



Courtesy Thermal Syndicate, Ltd.

Fused Silica Hydrochloric Acid Absorber for Making High-Purity Acid

further that at a high humidity the rate of attack increases with sulfur dioxide content of the air up to about 1 per cent sulfur dioxide, then decreases slightly, and finally rises sharply. This effect is explained by analysis of the corrosion products: those from atmospheres containing less than 1 per cent sulfur dioxide are basic; those from stronger mixtures contain an excess of free sulfuric acid (no sulfites were found in any case).

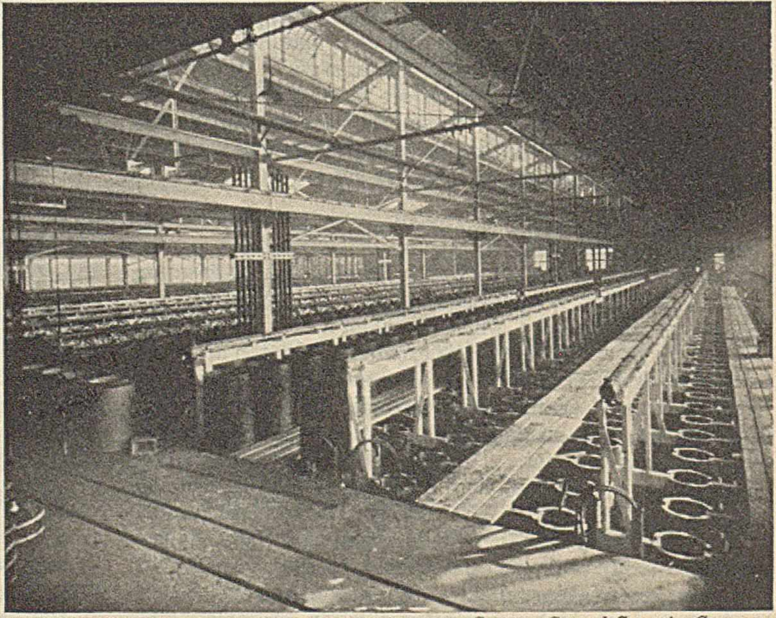
The same emphasis is placed on the necessary presence of moisture in the corrosion of power-plant equipment by flue gases (where sulfur oxides are again the active agent). Johnstone (*14*) has proved that the dew point of gases containing sulfur trioxide and water vapor is considerably above that of gases containing water vapor alone, and he has devised an ingenious dew-point apparatus (*13*), which is dependent on the very same phenomenon as is corrosion—the formation of an electrically conducting film. The presence of ferric sulfate also influences the condensation of moisture, and, to prevent corrosion, the actual temperature of the metal (not of the gas) must be above that at which an acid film condenses.

The essential factor, even in the rusting of iron, has recently been shown (*17*) to be a critical humidity of the atmosphere, determined by the gel structure of precipitated colloidal oxide (rust).

This first type of action is, then, intimately connected with the presence of moisture in the gases and is dependent on many of the same considerations as influence the corrosion in the presence of liquids.

The second general type of corrosion by gases is an effect of entirely different order of magnitude at ordinary temperatures, or else appears only at elevated temperatures. A metal exposed to a gas for which it has any affinity will soon become covered with a molecular layer of the compound; but, in order for action to proceed further, the gas must penetrate to lower layers. This diffusion is very slow at ordinary temperatures; consequently this type is often referred to as high-temperature corrosion, though in certain cases the same kind of action is noted at moderate temperatures. Pilling and Bedworth (*18*) enunciated the factors on which surface attack of metals depends: the dissociation pressure of the corrosion product (distinguishing, for example, the noble metals from the base); the ratio (molecular weight of compound multiplied by density of metal) divided by (molecular weight of metal multiplied by density of compound), which determines whether the compound forms a continuous protective layer over the underlying metal; the coefficient of thermal expansion of the compound compared with that of the metal; the plasticity, strength, and adhesion of the compound, and, of course, its volatility; the saturation concentration of the gas in the compound; and the specific diffusivity of the gas through it. If the compound is non-volatile and forms a continuous coating over the metal, the rate of attack is governed by a well-defined law, since the amount of gas diffusing decreases with increasing thickness of the layer: the extent of the attack increases with the square root of the time of exposure. This parabolic rate is characteristic of high-temperature surface attack, but the same effect is seen in certain low-temperature corrosion results. Vernon (*22*) found that the attack of hydrogen chloride and of hydrogen sulfide on steel followed the same parabolic law. In the case of hydrogen sulfide, moreover, Vernon found that the rate of attack was the same whether the specimen was polished or rough, showing that the attack was uniform over the surface and not dependent on local centers of activity, as in the case of sulfur dioxide where rough specimens corroded much more rapidly.

The disintegration of metals under direct gaseous attack (type 2*b*) depends on quite a different set of factors, concerning which not so much is known at present. When no protective compound is formed at the surface, gas at high temperatures may diffuse into metal, and, if it there reacts to form compounds of different density or other properties (as by



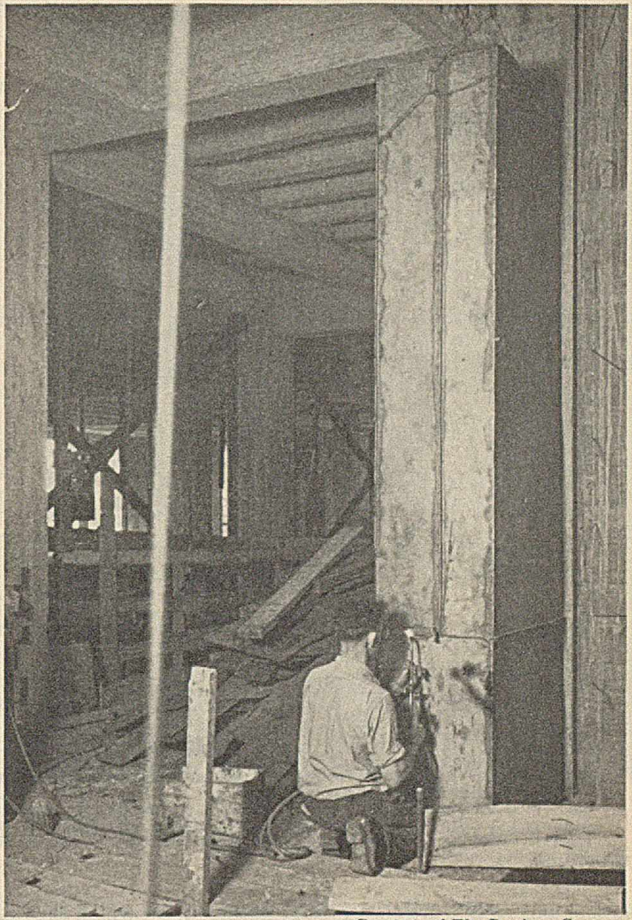
Courtesy General Ceramics Co.

Stoneware Electrolytic Cells and Stoneware Chlorine Piping reduction of oxides or carbides), the metal may lose the strength which it owed to these ingredients. Oxide inclusions are often concentrated at the grain boundaries, and attack may lead to fissures between adjacent grains, or "intergranular embrittlement."

1. Moist Gases

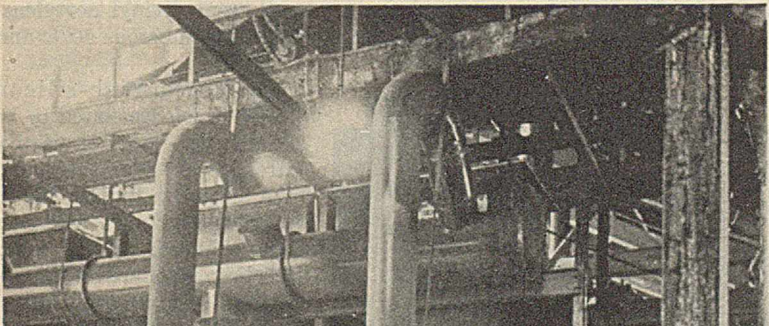
The selection of resistant materials for handling moist corrosive gases is in general dictated, as mentioned above, by the same considerations as govern selection for resistance to the same agents in aqueous solution. Previously published lists of available materials (*3, 5, 6, 11, 12, 23*) have been drawn on freely for the suggestions listed below under the common corrosive gases. Particular attention should be called to a valuable compilation (*1*), now available as a separate reprint, entitled "Tables of Chemical Compositions, Physical and Mechanical Properties, and Corrosion-Resistant Properties of Corrosion-Resistant and Heat-Resistant Alloys." Table I has been compiled from this source and shows typical analyses of metals recommended by the manufacturers as resistant to the corrosive agents cited. For resistance to corrosive gases, only those should be considered in general which are recommended as resistant to the reagent at all dilutions and all temperatures, since the gases are more likely to be handled warm than the solutions. This has been the basis of selection for inclusion in the table.

Moist Sulfurous Gases. Emphasis is laid on "moist," since, in the absence of moisture, corrosion is not severe. The moist gases, particularly when warm and in the presence of oxygen, present a difficult problem for which various solutions are proposed. Lead is available for moderate temperatures, and for applications where strength is not required. It has, therefore, been included in the table although recommended by the manufacturer only for room temperature. The high nickel-silicon steels, the high chromium and high chromium-nickel irons are resistant in the presence of ferric sulfate, which seems to exert a protective influence (*14*). Otherwise recourse must be taken to some of the more resistant materials, such as high silicon-iron alloys; enamel lining (enamel-covered tubes are used in one type of boiler economizer); brick lining (as in the flues of sulfuric acid plants between the cast-iron coolers and the first scrubbing tower); or glass, fused silica, or wood. Carbon (graphite) also is useful for Cottrell precipitator tubes or tower packing; it must not be used under oxidizing conditions. Promising results have been obtained (*14*) with one type of resinoid enamel as a protective coating in the presence of moist sulfur dioxide at 200° F. (93° C.).



Courtesy of The Duriron Co.

Durimet Fume Duct Installed from Battery Room in a Telephone Building



Courtesy U. S. Rubber Co.

Rubber-Lined Flue Installation for Carrying Corrosive and Erosive Gases

Moist Nitrous Gases. It is no longer news that ductile alloys are now available which are satisfactorily resistant to nitric acid and moist oxides of nitrogen. These alloys, known under various trade names, are comprised under the high chromium and high chromium-nickel groups, and are obtainable in practically any form; centrifugal blowers are in use, but there is difficulty in lubricating bearing surfaces of high-chrome alloys. These alloys should, however, never be used where there is the possibility of halogen compounds being present, since they are rapidly attacked by mixtures of nitric and hydrochloric acids (or other halogen acids). This is particularly dangerous in a nitric acid absorption system, since the halogen acid builds up to a high concentration in the intermediate strengths of nitric acid, owing to the reaction of the halide with the more concentrated nitric acid and the hydrolysis by the weaker acid of the nitrosyl halide so formed. These alloys should, therefore, not be used for recovery of nitrogen oxides from natural nitrate containing chlorine and iodine. There is also some question as to the resistance of certain alloys to acids containing lower oxides of nitrogen;

Table I. Typical Composition of Alloys Recommended for Resistance to Corrosion (*1*)

Fe %	C %	Cr %	Ni %	Mo %	Si %	Cu %	Mn %	W %	Ta %	Pb %	Al %	Sb %
MOIST SULFUR DIOXIDE[a]												
Bal.	0.15	19.0	9.0	1.5	0.35	1.5	..	...	...	...	...	...
Bal.	0.20	19.0	10.0	3.25	..	...	..	...	...	...	...	...
Bal.	0.30	11.0	36.0	...	0.20	...	1.5	...	...	...	...	...
Bal.	0.35	14.0	...	...	0.80	...	0.35	...	...	...	...	...
Bal.	0.18	21.5	11.5	...	1.05	...	0.70	...	...	...	...	...
Bal.	0.12	17.5	...	...	0.85	...	0.50	...	...	...	...	...
Bal.	0.15	18.0	8.5	...	0.75	...	0.50	...	...	...	...	...
Bal.	..	28.5	...	...	..	...	..	...	...	...	...	...
6.0	..	14.0	58.0	17.0	..	...	..	5.0	...	...	...	...
..	..	..	...	...	..	...	..	...	100	...	...	...
..	..	..	...	...	..	...	..	...	...	94.0	...	6.0
..	..	..	...	...	..	0.06	..	...	...	99.93	...	...
MOIST NITROUS GASES[b]												
Bal.	0.20	18.5	8.5	...	..	...	0.50	...	...	...	...	...
Bal.	0.12	18.5	...	...	0.40	...	0.40	...	...	...	...	...
Bal.	0.15	19.0	9.0	1.5	0.35	1.5	..	...	...	...	...	...
Bal.	0.20	25.0	17.5	...	1.5	...	..	...	...	...	...	...
Bal.	0.20	19.0	10.0	3.25	..	...	..	...	...	...	...	...
Bal.	0.35	19.5	7.25	...	1.4	...	0.55	4.0	...	...	...	...
Bal.	0.25	28.5	...	...	0.25	...	0.40	...	...	...	...	...
Bal.	0.18	21.5	11.5	...	1.05	...	0.70	...	...	...	...	...
6.0	..	14.0	58.0	17.0	..	...	..	5.0	...	...	...	...
Bal.	..	25.0	60.0	...	..	8.0	..	...	...	...	...	...
..	..	..	...	...	..	...	..	...	100	...	...	...
MOIST HYDROCHLORIC ACID VAPORS[c]												
Bal.	0.30	11.5	60.5	...	0.65	...	1.25	2.5	...	...	...	...
6.0	..	14.0	58.0	17.0	..	...	..	5.0	...	...	...	...
20.0	..	..	58.0	20.0	..	...	2.0	...	...	...	...	...
..	..	..	...	...	..	...	..	...	100	...	...	...
MOIST CHLORINE[d]												
Bal.	0.15	19.0	9.0	1.50	0.35	1.50	..	...	...	...	...	...
6.0	..	14.0	58.0	17.0	..	...	..	5.0	...	...	...	...
..	..	..	...	...	..	...	..	...	100	...	...	...
MOIST HYDROFLUORIC ACID VAPORS, COLD[e]												
..	..	..	...	...	..	0.06	..	...	...	99.93	...	...
4.0	..	..	...	...	..	88.0	..	...	...	...	8.0	...
Bal.	..	..	60.0	25.0	..	8.0	..	...	...	...	...	...

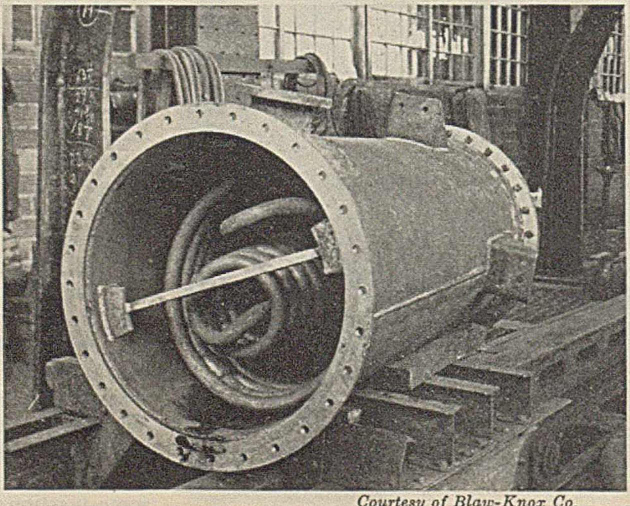
[a] Alloys taken from column headed "Moist Sulfurous Atmosphere" (*1*).
[b] Alloys taken from column headed "Nitric Acid" (*1*); recommendations for all concentrations at room and some higher temperature.
[c] Alloys taken from column headed "Hydrochloric Acid" (*1*); same recommendations.
[d] Alloys taken from column headed "Chlorine in Aqueous Solution" (*1*); same recommendations.
[e] Alloys taken from column headed "Hydrofluoric Acid" (*1*), and are the only ones unqualifiedly recommended by the manufacturers; none are recommended for hot solutions.

anomalous results are occasionally obtained, for which the full explanation has not been found.

Moist nitrous gases containing halogen acids can only be handled in ceramic ware or other highly resistant materials, such as iron-silicon alloys or tantalum. Ceramic-ware towers are standard for recovery of nitrogen oxides from natural nitrate. Stoneware or silicon-iron steam-jet exhausters are used; stoneware fans can also be obtained (*15*).

Mixtures of nitrous and sulfurous gases constitute a common problem in the chamber sulfuric acid plant. Chemical lead for construction of the flues, and antimonial hard lead for fans have been the usual solution, though the cost of maintenance and replacement indicates that there is still something to be desired. Some plants minimize trouble with the fan by designing the system for very low pressure drop and by drawing the gases through the entire system by means of the exit fan; the wear on the hot fan is thereby eliminated.

Moist Halogen Acid Vapors. Moist hydrochloric acid vapor in air represents one of the most severe corrosive conditions encountered. Until recently, metals other than platinum or tantalum were not available for this service. Some alloys are now on the market, of composition given by the table, which show promise in resisting hydrochloric acid, and, where it is desirable to use a metal, samples should be exposed under service conditions to determine the probable life. A number of other alloys are recommended for cold dilute acid and might be tried under these conditions, but too much should not be expected of them.



Courtesy of Blaw-Knox Co.

Chrome-Iron Condenser

Protective linings are of use in handling hydrochloric acid vapors, particularly linings of soft or hard rubber, provided the temperature does not exceed 150–200° F. (65–95° C.). Recently developed derivatives of vinyl-acetylene (*4*, *16*) may find application as plastic linings for this service, particularly the synthetic drying oils produced from divinyl acetylene, which exhibit remarkable resistance to numerous acids and other reagents.

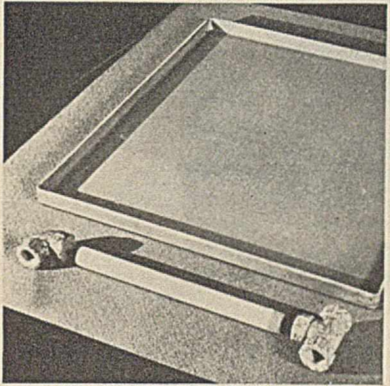
Aside from high-silicon irons, which are stated to be somewhat attacked by strong hydrochloric acid, and the alloys mentioned above, only non-metallic materials can be used. Fused silica has been standard for this application; glass and stoneware, of course, are also used. A newcomer in this field, for moderate temperatures, is piping, etc., of a molded phenol-formaldehyde resin.

Hydrofluoric acid, moist, is an even more difficult problem than hydrochloric, although, when it is substantially anhydrous, copper or even iron can be used. In the absence of oxygen, copper can be used for moist vapors. Not a single alloy or metal is recommended for hot hydrofluoric acid. The rare metals, such as platinum, are useful; but those shown in Table I are recommended only for the cold acid. Ceramic materials are ruled out, but the phenol-formaldehyde product should be serviceable. Wood is also used.

OTHER GASES. Moist chlorine likewise is to be avoided if possible, rather than handled. Where not possible, a few metals are listed as recommended by the manufacturers. Otherwise, non-metals, hard rubber, ceramic materials, and the like, are called for. Standard practice in compressing electrolytic chlorine is to dry it in stoneware towers by scrubbing with sulfuric acid and to compress it with a turbine pump sealed with sulfuric acid.

Moist hydrogen sulfide, as encountered in the oil industry, is combated by the use of high chrome and high chrome-nickel irons, aluminum, and aluminum-coated iron. The use of light sheet-aluminum coatings for oil storage tanks has been described (*9*). For small concentrations of hydrogen sulfide in air, a satisfactory life can be obtained by the use of asphalt-type paints on steel equipment.

Moist ammonia gas can be handled in steel pipes, with standard ammonia fittings and valves—never brass. Nickel and nickel alloys are serviceable at low temperatures, but at moderately elevated temperatures they are rapidly attacked in the presence of oxygen and moist ammonia.

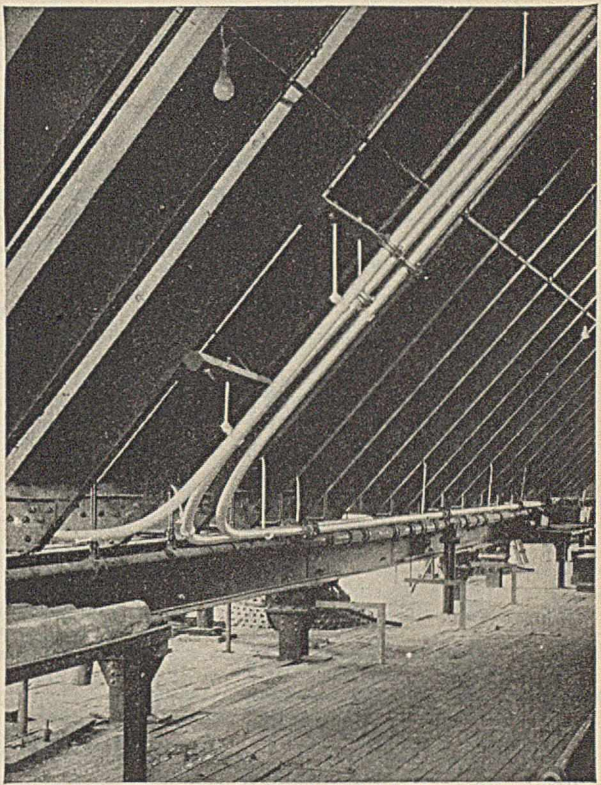

Courtesy of The Bakelite Corporation

CONTINENTAL-DIAMOND FIBRE CHEMICAL APPARATUS PARTS

2 (*a*). HIGH-TEMPERATURE SURFACE ATTACK

The factors controlling resistance of metals to direct gaseous attack are quite different from those for ordinary corrosion, and no other fund of information can be drawn on except experience with the specific problems. The controlling properties are those of the surface compound formed rather than of the metal, and progress has been more or less empirical.

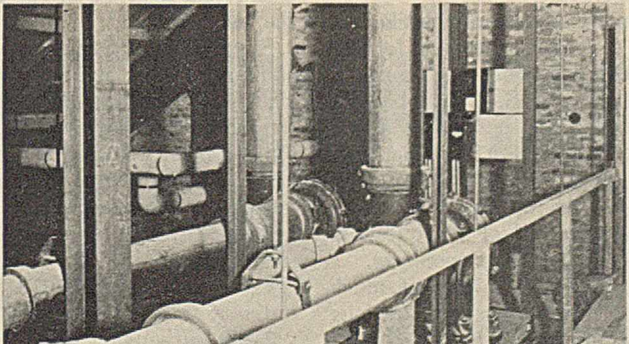
AIR. At high temperatures air is an active reagent, oxidizing the base metals as rapidly as the oxygen can diffuse at the temperature. Progress has been made, however, in meeting the demand for heat-resistant alloys. Some of the work in this field has been included in the important symposium of papers held under the auspices of the American Society for Testing Materials and the American Society of Mechanical Engineers (*7*, *19*). Chromium is the chief alloying element in heat-resistant metals, the necessary percentage increasing with the temperature of operation, up to 80 per cent chromium, 20 per cent nickel, for the highest temperature covered by base metals. Table II gives typical analyses of alloys recommended for high-temperature service, with the temperature stated by the manufacturer as the maximum for continuous operation. The source is the same as Table I (*1*).


Courtesy of Babcock and Wilcox Co.

SEAMLESS NIROSTA KA2 RELIEF LINES FROM PULP DIGESTERS

Even nitrogen at high temperatures is not wholly inert, and some is absorbed by molten steel (*8*, *20*).

It should be stated that tantalum burns when heated in air above 350° C.; and molybdenum, when used for high-temperature resistance furnaces, must be kept in high vacuum to prevent oxidation. Even platinum oxidizes at high temperatures, although alloying it with rhodium diminishes the rate.


Courtesy of The Duriron Co.

DURIRON FAN INSTALLATION FOR EXHAUSTING LABORATORY HOODS AT VILLA NOVA COLLEGE

HOT SULFUROUS GASES. The presence of sulfurous gases at high temperatures increases the rate of attack, and the list of metals recommended for this service is not so long as that for air or simply oxidizing fuel gases. There is, moreover, some inconsistency in the recommendations of different manufacturers of the same alloy composition for this particular application. In addition to the alloys listed, an alloy recommended consists of iron with 15 per cent aluminum. A recent publication (*10*) claims that the addition of aluminum to the

Table II. Typical Composition of Alloys Recommended for Resistance to Direct Gaseous Attack (*1*)

Max. Temp. Recommended ° C.	Composition												
	Fe %	C %	Cr %	Ni %	Mo %	Si %	Cu %	Mn %	W %	Sn %	Co %	Ti %	Al %
ATTACK BY AIR AND OXIDIZING FUEL GASES[a]													
500	..	..	..	29.0	..	...	70.0	..	...	1.0	..	...	..
500[b]	Bal.	Bal.	..	69.0	..	Bal.	28.0	Bal.	...	...	..	...	..
540	Bal.	0.35	14.0	...	..	...	..	0.30	...	...	..	...	..
595	Bal.	0.12	13.0	2.0	..	...	..	..	...	...	..	...	..
700	6.5	..	..	72.0	..	...	..	..	...	...	18.0	2.5	0.50
700[b]	...	..	..	99.2	..	...	..	..	...	...	..	...	..
760[b]	Bal.	0.40	8.0	20.0	..	1.0	..	0.75	...	...	..	...	..
760[b]	Bal.	0.08	13.5	...	..	0.50	..	0.50	...	...	..	...	..
800[b]	20.0	..	..	58.0	20.0	...	..	2.0	...	...	..	...	..
800[b]	..	..	..	85.0	..	10.0	3.0	..	...	...	..	...	2.0
800[b]	Bal.	0.30	11.5	60.5	..	0.65	..	1.25	2.5	...	..	...	..
815	Bal.	0.62	17.0	...	..	0.50	..	0.35	...	...	..	...	..
815[b]	Bal.	0.30	11.0	26.5	..	1.50	..	1.50	...	...	..	...	..
815[b]	Bal.	0.30	11.0	36.0	..	0.20	..	1.50	...	...	..	...	..
870[b]	Bal.	0.15	18.0	8.5	..	0.75	..	0.50	...	...	..	...	..
900[b]	Bal.	0.15	19.0	9.0	1.5	0.35	1.50	..	...	...	..	...	..
900[b]	Bal.	0.35	19.5	7.25	..	1.40	..	0.55	4.0	...	..	...	..
900[b]	Bal.	..	15.0	35.0	..	...	..	..	...	...	..	...	..
925[b]	Bal.	..	25.0	...	..	...	..	..	...	...	..	...	..
950[b]	Bal.	0.47	14.0	26.5	..	1.35	..	1.30	3.40	...	..	...	..
980[b]	Bal.	..	20.0	8.0	..	...	..	..	...	...	..	...	Bal.
980[b]	Bal.	..	25.0	60.0	..	...	..	8.0	...	...	..	...	..
1000[b]	Bal.	0.12	15.0	60.0	..	...	..	..	...	...	..	...	..
1000[b]	...	..	..	45.0	..	...	55.0	..	...	...	..	...	..
1000	Bal.	..	30.0	...	..	...	..	..	15.5	...	50	...	..
1000	Bal.	..	30.0	...	..	...	..	..	4.0	...	65	...	..
1000	Bal.	..	30.0	...	..	...	..	..	8.0	...	60	...	..
1000[b]	6.0	..	14.0	58.0	17.0	...	..	..	5.0	...	..	...	..
1010[b]	Bal.	0.5	18.0	38.0	..	2.0	..	1.12	...	...	..	...	..
1035[b]	Bal.	0.2	17.0	25.0	..	2.5	..	..	...	...	..	...	..
1095[b]	Bal.	0.2	25.0	17.5	..	1.5	..	..	...	...	..	...	..
1095	Bal.	0.8	19.0	65.0	..	2.0	..	2.0	...	...	..	...	..
1150[b]	Bal.	0.6	22.0	23.0	..	1.8	..	0.5	...	...	..	...	..
1150[b]	...	..	20.0	80.0	..	...	..	..	...	...	..	...	..
ATTACK BY SULFUR GASES[c]													
540	Bal.	0.15	18.2	8.5	..	0.75	..	0.50	...	...	..	...	..
760	Bal.	0.08	13.5	...	..	0.50	..	0.50	...	...	..	...	..
815	Bal.	0.10	17.5	...	..	0.88	..	0.50	...	...	..	...	..
925	Bal.	..	25.0	...	..	...	..	..	...	...	..	...	..
ATTACK BY HYDROGEN, NITROGEN, AND AMMONIA[d]													
480	Bal.	0.07	18.5	8.5	..	...	..	..	...	...	..	...	..
540	Bal.	0.20	25.0	17.5	..	1.5	..	..	...	...	..	...	..
650	Bal.	0.30	11.5	60.5	..	0.65	..	1.25	2.5	...	..	...	..
705	Bal.	0.20	19.0	10.0	3.25	...	..	..	...	...	..	...	..
785	Bal.	0.40	8.0	20.0	..	1.00	..	0.75	...	...	..	...	..
900	Bal.	..	15.0	35.0	..	...	..	..	...	...	..	...	..
1000	..	..	..	45.0	..	...	55.0	..	...	...	..	...	..
1000	Bal.	0.12	60.0	15.0	..	...	..	..	...	...	..	...	..
1010	Bal.	0.50	18.0	38.0	..	2.0	..	1.12	...	...	..	...	..
1035	Bal.	0.20	17.0	25.0	..	2.5	..	..	...	...	..	...	..
1095	Bal.	0.50	20.0	67.0	..	1.75	..	1.32	...	...	..	...	..

[a] Alloys are listed under the lowest maximum operating temperature recommended by any manufacturer for material of substantially the same composition.

[b] Recommended for oxidizing fuel gases at the same temperature.

[c] Only those alloys recommended for H_2S, SO_2, and SO_3 are included; the temperature is the lowest recommended by any manufacturer for substantially the same composition.

[d] Taken from column with this heading (*1*); the temperatures given are the lowest recommended by any manufacturer for any of the three gases for substantially the same alloy composition. Note that the metals should not be used at high pressure at these temperatures.

chromium-nickel alloys increases greatly their resistance to sulfur-bearing gases at high temperature.

Hot Halogen Gases. Not many oxides are volatile, but chlorides often have appreciable vapor pressures, and for this reason most metals are rapidly attacked by hot gases containing chlorine or hydrogen chloride. The A. S. T. M. tables (*1*) do not list any metals recommended for these gases above 300° C. One of the present writers (T. H. C.) found nickel to be fairly satisfactory for a mixture containing a chlorinated hydrocarbon and air at temperatures up to 400°, where alloys containing iron or copper were out of the question. Silica or other vitreous materials are generally necessary.

Hot Oxides of Nitrogen. These gases are not much more corrosive than oxygen at the same temperature (as long as the dew point is not reached).

Hot Ammonia-Air Mixtures. Not so much because of the effect of the gases on the metals as on account of the catalytic effect of the metals on the gases, all except aluminum and nickel are to be avoided.

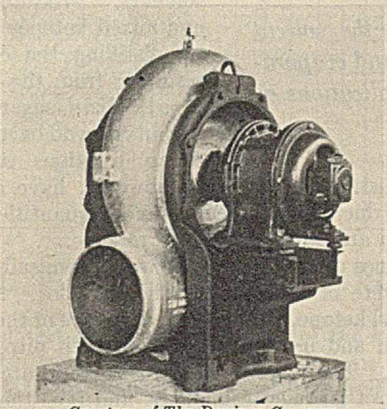
Hot Ammonia. This gas at atmospheric pressure is included on account of its effect in nitriding. This is now practiced intentionally to produce a hard surface on steel, and is applied best on special alloys generally containing aluminum. For catalyst tubes in ammonia "crackers," ordinary steel has been found to give a useful life, being somewhat protected by the catalyst.

Superheated Steam. There is a growing literature on equipment for high-pressure highly superheated steam. Though the emphasis is generally on the physical properties of the material, there is recognition of the fact that steam does tend to react with metals, such as iron at high temperatures, and is definitely erosive if not corrosive when flowing at high velocity. Nickel-copper alloys, high-chrome irons, and latterly, nitrided alloys have been used to meet these requirements.

Carbon Monoxide. At high pressures on iron and at ordinary pressure on nickel, carbon monoxide reacts to form volatile carbonyls. It is, therefore, generally brought in contact only with copper when heated under pressure. At high temperatures carbon monoxide is acted on catalytically by iron oxide, forming carbon dioxide and carbon, a deposit of which may "grow" to large proportions.

2 (*b*). Disintegration Attack

This problem has come into prominence in the development of synthetic processes involving the use of hydrogen at elevated pressures and temperatures, and is limited largely to this one gas or to those which generate it (ammonia, for example). While Table II lists a number of alloys recommended for hydrogen, nitrogen, and ammonia at the temperatures stated, these alloys could not be used under high pressure to a temperature anywhere approaching the limits set. Not much appears to have been published on this subject since the work of Vanick (*21*), who found that iron was attacked as was also nickel and its alloys, and that only a nickel-chromium-aluminum alloy and an iron-nickel-chromium were promising. The problem has been met in practice by the use of internal heat exchangers and the avoidance of high temperature. Work is continuing, however, and developments can be looked for in alloys resistant at higher temperatures (*2*).



Courtesy of The Duriron Company

New Type Fan with One-Piece Housing. All parts touched by fumes are Duriron

In conclusion, the authors would add that the avoidance of trade names in the discussion of alloys should not be construed as disparaging the use of trade names as a mark of standard quality but has been adopted only to avoid confusion in the use of different names for substantially the same analysis. Some confusion has arisen from time to time as a result of change in trade name by manufacturers for the same alloy. It would be an advantage to the user if the composition were frequently mentioned in advertising literature.

Acknowledgment

Other members of the chemical and engineering departments and members of other departments of E. I. du Pont de Nemours & Company have contributed information in the preparation of this article, and their assistance is gratefully acknowledged.

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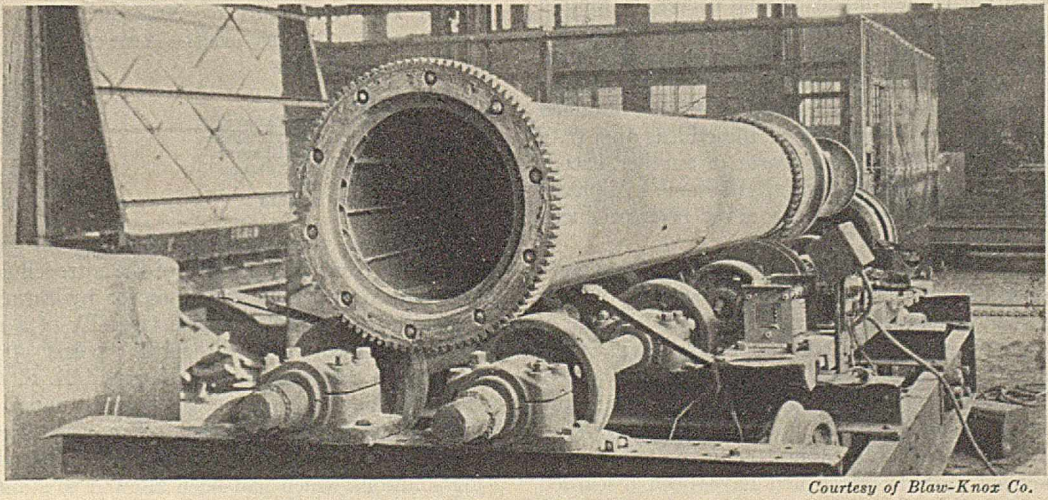

Courtesy of Blaw-Knox Co.

Electric-Welded Chrome-Iron Rotary Retort

Aliphatic Ketones as Solvents

J. G. Park and H. E. Hofmann, *Stanco Inc., Elizabeth, N. J.*

THE PURPOSE of this paper is to present a systematic study of the aliphatic ketones—acetone, methyl ethyl, methyl butyl, and methyl amyl—from the standpoint of their inherent properties.

The properties discussed include the solvent power, solubility of oils and resins, and evaporation rates, together with suggested applications as determined by practical tests.

THE story of the rapid growth of the use of nitrocellulose lacquers as industrial finishes is one familiar to every protective-coating chemist. From 1922 to 1929 the industry was constantly faced with the specter of a solvent shortage. Since 1929 this apparition has disappeared, and the demand is now for cheaper and better solvents in order that nitrocellulose lacquer may enlarge its scope of usefulness and enter new fields.

In discussing the relation of constitution to the properties of lacquer solvents, Calvert (*2*) says, after pointing out the nature of nitrocellulose: "It should not be surprising . . . . . . that pyroxylin solvents of present commercial importance are oxy-compounds usually containing either a carbonyl group, as in an ester or a ketone, or an alcohol and ether group, as in the mono-ethers of ethylene glycol." Other writers have alluded to the fact that ketones as a class are excellent nitrocellulose solvents, but individuals with the correct properties have not been available.

Table I. Physical Properties of Aliphatic Ketones

(Data taken mostly from International Critical Tables)

	Acetone	Methyl Ethyl Ketone	Methyl Propyl Ketone	Methyl Butyl Ketone	Methyl Amyl Ketone
Molecular weight	58	72	86	100	114
Boiling point (760 mm.), ° C.	56.1	79.6	102	127.2	150.2
Specific gravity $\frac{20° \text{ C.}}{4°}$	0.7915	0.8050	0.8089	0.8209	0.8269
Refractive index (20° C.)	1.3587	1.3791	1.3895	1.4024	1.4110
Viscosity, centipoises (25° C.)	0.316	0.401	0.473	0.584	0.766
Vapor pressure (20° C.)	184.8	77.5	30	10	3.6
Flash point (closed cup), ° F. (° C.)	2 (−16.7)	19 (−7.2)	45 (7.2)	73 (22.8)	106 (41.1)
Latent heat, cal./gram	125	106	91	83	83
Specific heat, cal./gram	0.527	0.550	....	0.553	....
Dielectric constant	21.4	18.4	15.4	12.2	....
Surface tension (20° C.)	23.7	24.6	25.2	25.5	....

No data are available for the spaces indicated by leaders.

The use of higher ketones as solvents in nitrocellulose compositions is described in a patent granted to Seher in 1892 (*4*). Mention is here made, among others, of methyl ethyl, methyl propyl, methyl butyl, and methyl amyl ketones. Since that time many other patents have been issued, covering the use of a ketone or ketones in some special type of product, or covering the use as solvents of ketones obtained by various processes (*1*). Very few of these ideas appear to have been put into practice for one reason or another, except with respect to acetone and methyl ethyl ketone. Aliphatic ketones of higher boiling points have never been produced on a commercial scale.

Several ketone solvents have been available in moderate quantities for some time, but each has at least one distinct disadvantage which removes it from the consideration of lacquer manufacturers. These include principally: cyclohexanone, which is too high-boiling and too expensive; diacetone alcohol, which readily decomposes into acetone; and mesityl oxide, which contains an unsaturated bond, and is therefore unstable. The only other source of ketones has been the so-called acetone oils which have been discarded on account of their bad odors.

Another source of ketones is described by Desparmet (*3*) in a recent article in which he also refers to the advantages of ketones as nitrocellulose solvents. Mixtures of simple and mixed ketones are obtained by distilling the calcium salts resulting from the fermentation of alkaline sugar solutions by butyric acid bacteria. These sugar solutions are prepared from sawdust. The products, however, have an empyreumatic odor, due to the presence of small quantities of pyridine bases which are quite difficult to remove.

The ketones used in this work were chemically pure products and were of a pleasant ethereal odor. Acetone and methyl ethyl ketone, the first two members of the series, have been known and used in connection with nitrocellulose for some time. The three higher members are newcomers to the field of lacquer technology, and it is their properties that are being studied here. These ketones were prepared from the secondary alcohols, and therefore it may be stated that their availability is assured. The compounds are colorless mobile liquids having the physical properties shown in Table I.

SOLVENT POWER

The most interesting property of a solvent is its solvent power. The first investigation made of the ketones was upon the solvent action of these compounds on the various types of cellulose compounds. Cellulose acetate is readily soluble in acetone. Some grades are soluble in methyl ethyl ketone, while practically all are soluble in a mixture of the ketone with a small proportion of ethyl alcohol. The ketones higher than methyl ethyl do not dissolve cellulose acetate even in the presence of alcohol, but are latent solvents when used in conjunction with certain solvent plasticizers. This action is similar to that of camphor and alcohol upon cellulose nitrate. The cellulose ethers are soluble in all of the ketones, but probably not as readily as in the coal tar hydrocarbons.

Table II. Viscosities of Nitrocellulose Solutions

(20% solutions at 25° C.)

Solvent	Viscosity *Poises*
Acetone	1.4
Methyl ethyl ketone	2.0
Methyl propyl ketone	3.4
Methyl butyl ketone	7.5
Methyl amyl ketone	12.0
Ethyl acetate	3.0
n-Butyl acetate	9.1

The ketones are excellent solvents for nitrocellulose, judged both from the viscosity of the nitrocellulose solutions they produce and their tolerance for hydrocarbons. As it is generally recognized that the viscosity of a nitrocellulose solution is indicative of the solvent power of the solvent, a 20 per cent solution of dry half-second R. S. nitrocellulose was prepared with each of the ketones under observation, as well as with butyl acetate. The viscosities were then determined at 25° C. by means of a MacMichael viscometer, using solutions which had been allowed to stand for several weeks after being prepared.

It will be noted that in this series of ketones, as is the case in any homologous series of solvents, the solvent power decreases as the molecular weight increases.

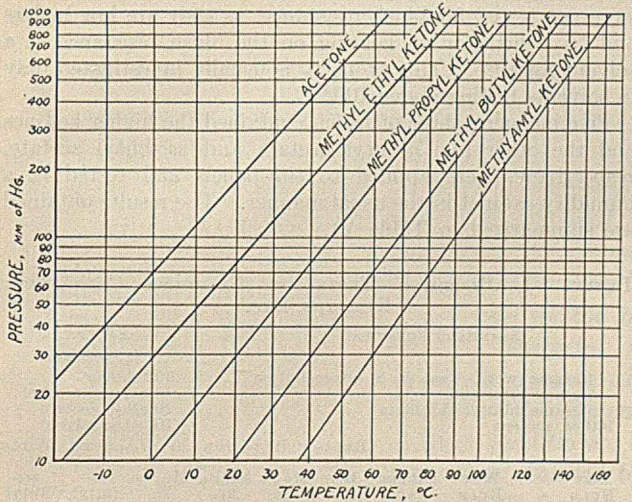

FIGURE 1. VAPOR PRESSURE OF ALIPHATIC KETONES

As a further test of the solvent power of the ketones, the dilution ratios were determined with toluene and with lactol spirits. Lactol spirits is a petroleum distillate boiling between 80° and 130° C. The method used for determining the dilution ratios is the classical one in which the solvent and non-solvent are so adjusted just before the end point is reached that the final concentration of nitrocellulose lies between 5 and 7 per cent. As pointed out by numerous authors, it is necessary to adjust the final concentration of nitrocellulose to the same value in a series of tests so that comparative results will be obtained. The final ratios of non-solvent to solvent by weight are given in Table III.

TABLE III. RATIO SOLVENT TO NON-SOLVENT

SOLVENT	DILUTION RATIO	
	Toluene	Lactol spirits
Acetone	4.75	0.625
Methyl ethyl ketone	4.5	0.73
Methyl propyl ketone	4.1	0.80
Methyl *n*-butyl ketone	4.0	0.80
Methyl *n*-amyl ketone	3.5	0.80
Ethyl acetate	3.6	1.2
n-Butyl acetate	3.1	1.3

TABLE IV. SOLUBILITIES OF SOLVENTS AND DILUENTS

	SOLVENT				
SUBSTANCE	Acetone	Methyl ethyl ketone	Methyl propyl ketone	Methyl butyl ketone	Methyl amyl ketone
Nitrocellulose	s	s	s	s	s
Cellulose acetate	s	s[a]	i	i	i
Ethyl cellulose	s	s	s	s	s
Water	s	ps	ss	vss	vss
95% alcohol	s	s	s	s	s
Petroleum spirits	s	s	s	s	s
All other solvents	s	s	s	s	s
Linseed oil	s	s	s	s	s
Tung oil	s	s	s	s	s
Castor oil	s	s	s	s	s
Mineral oil (tech. white)	i	s	s	s	s
Essential oils, etc.	s	s	s	s	s
Ester gum	ps	s	s	s	s
Dammar (whole)	ps	ps	ps	ps	ps
Bleached shellac	ps	ps	i	i	i
Kauri (chips)	s	s	s	s	s
Manila (hard)	s	s	s	s	s
Pontianac (nubs)	s	s	s	s	s
Glyptal-type resin	s	s	s	s	s
Amberol-type resin	i	s	s	s	s
Cumarone resin	i	s	s	s	s
Vinyl acetate resin	s	s	s	s	s
Rosin	s	s	s	s	s
Beeswax	i	i	vss	vss	vss
Paraffin wax	i	i	i	i	vss
Ceresin	i	i	i	vss	vss
Carnauba wax	i	i	i	i	i

[a]—in presence of alcohol
i—insoluble
s—soluble
ps—partially soluble
ss—slightly soluble
vss—very slightly soluble

It will be noted that the results obtained are parallel to those given in Table II, and it is evident from these data that the ketones have higher dilution ratios than the regular esters of corresponding boiling points, with the exception that, when petroleum naphthas are used, the dilution ratios of the ketones are somewhat inferior to those of the esters.

Investigation shows that the ketones are miscible in all proportions with the other solvents and diluents used in the lacquer industry. The solubility of the oils, waxes, and resins which are in common use are given in Table IV.

Methyl butyl and methyl amyl ketones show good compatability with ester gum and amberol resins in the presence of nitrocellulose, that is, the solution of nitrocellulose and resin is clear and gives a clear film. With methyl propyl ketone a small amount of plasticizer is necessary to produce a clear film, while with acetone and methyl ethyl ketone, a plasticizer and another solvent or diluent are necessary. Methyl ethyl ketone is approximately equivalent to ethyl acetate in its behavior with resins. All of the ketones show good compatability with blown castor oils and the glycerol–phthalic anhydride resins.

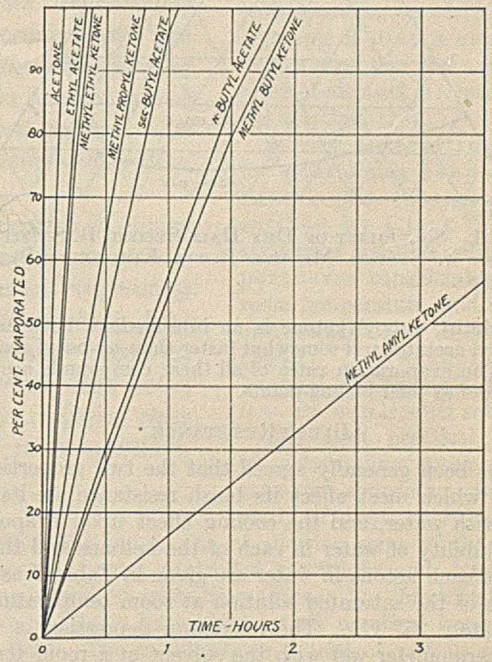

FIGURE 2. EVAPORATION RATES OF KETONES AND CERTAIN ESTERS
(Temperature, 18.5–19.5° C.)

VAPOR PRESSURE AND RATE OF EVAPORATION

The vapor pressures of the ketones were obtained from actual experimental determinations by the dynamic method. The logarithms of the values obtained were then plotted against the reciprocals of the absolute temperatures in accordance with the modified form of the Clausius-Clapeyron equation,

$$\log P = \frac{-K}{T}$$

and the curves obtained are shown in Figure 1.

The evaporation rates of the five ketones under investigation, as well as three of the common esters, were determined in the usual way. The results obtained are plotted graphically in Figure 2 and indicate the following facts:

1. Each ketone evaporates approximately twice as slowly as the one just before it in the series.

2. Methyl ethyl ketone matches ethyl acetate very closely in evaporation rate.
3. Methyl butyl ketone is a good match for *n*-butyl acetate.
4. Methyl amyl ketone evaporates very slowly, or about the same as *sec*-hexyl acetate. It is somewhat slower than butyl propionate or amyl acetate.

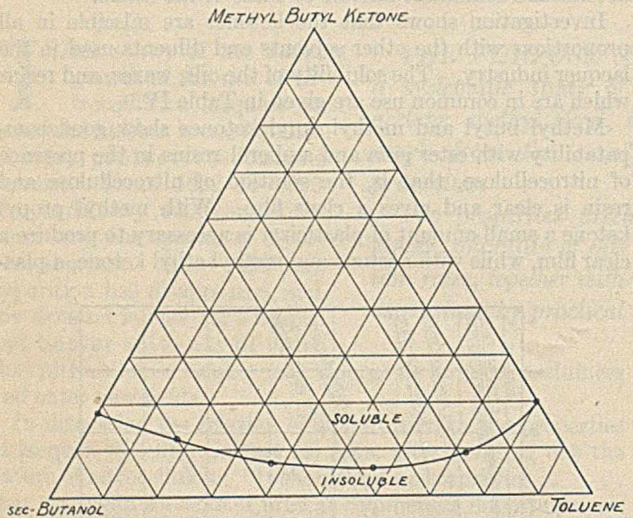

FIGURE 3. SOLUBILITY OF DRY HALF-SECOND R. S. NITROCELLULOSE IN SYSTEM METHYL BUTYL KETONE–*sec*-BUTANOL–TOLUENE

5. Methyl propyl ketone is an intermediate between ethyl and butyl acetates and somewhat faster than *sec*-butyl acetate.
6. The evaporation rates of all these compounds are in the same order as their boiling points.

BLUSH RESISTANCE

It has been generally agreed that the two properties of a solvent which most affect its blush resistance are its miscibility with water, and the cooling effect upon evaporation. The solubility of water in each of the ketones and the solubility of each ketone in water are given in Table V as a percentage of the saturated solution at room temperature (approximately 25° C.). The maximum depression of a wet-bulb thermometer wet with the solvent at a room temperature of 22.5° C. is also given.

TABLE V. SOLVENT PROPERTIES AFFECTING BLUSH RESISTANCE

SOLVENT	SOLUBILITY OF: Solvent in H_2O	SOLUBILITY OF: H_2O in solvent	WET-BULB DEPRESSION ° *C.*
Acetone	Infinite	Infinite	30.5
Methyl ethyl ketone	22.6	9.9	21.5
Methyl propyl ketone	6.0	3.6	12.0
Methyl butyl ketone	3.44	3.70	6.5
Methyl amyl ketone	1.95	2.15	3.0
Ethyl acetate	7.9	3.0[a]	21.5
n-Butyl acetate	2.3	2.4	6.5

[a] For C. P. product containing no alcohol; commercial material dissolves more water than this.

Some practical tests were conducted with the blush-resisting properties of the ketones under examination upon lacquers having the following composition:

STANDARD FORMULA	SOLVENT *% by volume*
14 grams (wet) 1/2 sec. R. S. nitrocellulose	60 toluene
5 grams ester gum	10 *n*-butyl alcohol
5 grams dibutyl phthalate	20 ethyl acetate
100 cc. solvent	10 other solvent

It is very difficult to obtain satisfactory data of an absolute nature concerning the actual blush resistance of a solvent. It is usually necessary to make comparative tests, using solvents of well-known properties as standards. The most universally used solvent having good blush resistance is *n*-butyl acetate, which has been used in these tests as a standard for comparison.

Acetone, which is miscible with water in all proportions, and methyl ethyl ketone, which dissolves considerable water, were not tested for blush resistance, as they are low boilers and have little or no bearing on the blush resistance of a solvent mixture. This property is usually investigated only in solvents boiling above 100° C.

Five lacquers, three of which contained the higher ketones and the other two *n*-butyl acetate and *sec*-butyl acetate, respectively, were applied to tin panels and tested in a humidity cabinet in the usual manner. The results obtained are summarized in Table VI.

TABLE VI. BLUSHING TESTS ON LACQUERS CONTAINING KETONES, ETC.

STANDARD FORMULA	SOLVENT *% by volume*
14 grams (wet) 1/2 sec. R. S. nitrocellulose	60 toluene
5 grams ester gum	10 *n*-butyl alcohol
5 grams dibutyl phthalate	20 ethyl acetate
100 cc. solvent	10 other solvent

DRY BULB	WET BULB	DIFFERENCE	RELATIVE HUMIDITY	BEHAVIOR OF LACQUER WHEN OTHER SOLVENT IS: Me Pr ketone	Me Bu ketone	Me Am ketone	*n*-Butyl acetate	*sec*-Butyl acetate
° *F.* (° *C.*)	° *F.* (° *C.*)	° *F.*	%					
87 (30.6)	85 (29.4)	2	92	–	–	–	–	–
87 (30.6)	84 (28.9)	3	89	–	–	–	–	–
86 (30)	83 (28.3)	3	89	–	–	–	–	–
82 (27.8)	79 (26.1)	3	88	–	–	±	–	–
87 (30.6)	83 (28.3)	4	85	–	–	±	±	–
86 (30)	82 (27.8)	4	85	–	±	+	±	–
85 (29.4)	81 (27.2)	4	85	–	±	+	±	–
83 (28.3)	79 (26.1)	4	85	–	±	+	±	–
87 (30.6)	82 (27.8)	5	81	–	±	+	±	–
85 (29.4)	80 (26.7)	5	81	±	+	+	+	±
84 (28.9)	79 (26.1)	5	80	±	+	+	+	+
87 (30.6)	81 (27.2)	6	77	+	+	+	+	+
85 (29.4)	79 (26.1)	6	77	±	+	+	+	+
87 (30.6)	79 (26.1)	8	70	+	+	+	+	+

– Bad blush; ± slight blush; + no blush.

While the results obtained hold only for lacquers of the general formula indicated, they are cited as comparative data.

USE OF KETONES IN THINNERS

The solubility of half-second nitrocellulose in ternary systems containing a solvent with *sec*-butyl alcohol and toluene was determined for methyl butyl ketone (Figure 3), as this solvent closely corresponds to *n*-butyl acetate.

CONCLUSION

In conclusion it may be stated that the uses of acetone are well known. Methyl ethyl ketone is recommended as a direct substitute for ethyl acetate in nitrocellulose lacquers, and as a medium-boiling solvent in cellulose acetate compositions. It might also well be used in paint removers, when a solvent is required of slower evaporation rate than acetone.

Methyl butyl ketone is recommended as a substitute for *n*-butyl acetate in all kinds of nitrocellulose lacquers. The methyl propyl and methyl amyl ketones may be used when ingredients of other evaporation rates are required. All have high dilution ratios, good blush resistance, and are compatible with all the resins. They are also stable to light, heat, and moisture, and do not turn dark upon aging.

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(3) Desparmet, *Cuir tech.*, 21, 56 (1928).
(4) Seher, A., U. S. Patent 470,451 (March 8, 1892).

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Evaporation Rates of Organic Liquids

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DATA USEFUL to the protective-coating technologist and various methods of determining rates of evaporation are discussed. The slopes of several evaporation curves are calculated and compared with that of n-butyl acetate; these slopes give concordant results only in the case of slowly evaporating liquids.

A simple method of determining evaporation rates is suggested which gives reproducible results on solvents whose evaporation rates are determined on different days with widely varying climatic conditions; these rates are compared with those obtained by the usual method. An approximate formula for predicting evaporation rates is given.

The evaporation phenomena existing in binary and ternary mixtures of the usual solvents are discussed. Several new constant-evaporating mixtures of alcohols and hydrocarbons have been determined. Two ternary mixtures, consisting of alcohol, hydrocarbon, and ester, which evaporate at essentially uniform rates and do not materially change in composition, are given.

A KNOWLEDGE of the rates of evaporation of organic solvents and mixtures of solvents, with or without non-volatile materials dissolved in them, is very important in the technology of protective coatings and in other fields where the value of the product depends to some extent on the evaporation of a volatile liquid. This is especially true in the cases of spirit varnishes, cellulose ester lacquers, synthetic resin varnishes, and similar materials. The need for reliable information concerning the rates of evaporation of solvents has long been recognized, and this field has been studied to some extent by chemists in the lacquer industry, but the data obtained have not been of such a nature that they can be readily expressed on paper except by means of a graph showing comparative evaporation curves of various solvents.

Considerable study has been devoted to the evaporation of liquids, chiefly water, in still air and in a current of gas, in various types of apparatus. This work is summarized in Volume V of International Critical Tables, but very few of the data are of interest to the protective-coatings technologist.

Early in the development of nitrocellulose lacquers it was found that the evaporation rates of the solvents used were not proportional to the boiling points, as is shown in Table I, where a few of the commonly used solvents are arranged in order of their boiling points and rates of evaporation.

TABLE I. COMMONLY USED SOLVENTS

ORDER OF BOILING POINTS	TEMP. ° C.	ORDER OF EVAPORATION RATES
Acetone	56.1	Acetone
Ethyl acetate	77.1	Ethyl acetate
Ethyl alcohol	78.2	Benzene
Benzene	80	Toluene
Toluene	110.5	Ethyl alcohol
n-Butyl alcohol	117.7	*n*-Butyl acetate
n-Butyl acetate	126.5	Xylene
Amyl alcohol	130	*n*-Butyl alcohol
Xylene	139	Amyl alcohol

It will be seen from Table I that the evaporation rates are not in the same order as the boiling points of the solvents. Those compounds containing a hydroxyl group evaporate much more slowly than compounds of the same boiling point not containing the hydroxyl group. The classification of solvents as low-boiling, medium-boiling, and high-boiling is therefore not strictly indicative except in a general way.

METHODS OF DETERMINING EVAPORATION RATES

A favorite method of determining evaporation rates, and one used by many investigators, is that in which air is passed over the surface of the liquid contained in a flask immersed in a constant-temperature bath. The humidity and the velocity of the air can be controlled, as well as the temperature of the entire apparatus; but the results depend upon whether the air inlet is parallel to, or perpendicular to, the liquid surface. This method has been adapted to industrial use in connection with gasoline, naphthas, etc. A sample of 10 cc. is evaporated in this way, and the number of liters of air used is a measure of the volatility (*15*).

A very interesting device for determining evaporation rates is the "secometer" described by Clark (*2*). This apparatus is useful only at temperatures considerably above room temperature, and for high concentrations of the vapor (water). The author has attempted unsuccessfully to adapt it to use with lacquer solvents.

The most practical method of determining evaporation rates in connection with the study of protective-coating solvents is the simple one of allowing some of the solvent to evaporate under controlled conditions and determining the loss of weight with time (Figure 1). Modifications of this method have been used by all practical investigators in the field. The modifications consist of various weighing devices, containers of various kinds for the liquids being tested, and a few methods of controlling the velocity and temperature of the air.

Besides the ordinary analytical balance, the Jolly spring balance and several specially designed balances have been suggested (*8*). The containers most often used are seamless covers for friction-top cans. These are quite uniform as to dimensions, but the various writers have failed to mention the size of the containers used by them. Bridgeman suggests an aluminum pan with slight depression in the center of the bottom (*1*). Most determinations of evaporation rates have been made in the "still air" of a laboratory, but Wilson and Worster (*17*) describe a small air tunnel which should be very satisfactory for controlling the velocity of the air over the surface of the liquid.

This experimental method has several disadvantages if exact information is to be obtained, although it is admittedly satisfactory for practical purposes:

(1) On account of physical limitations only a few liquids can be tested at one time.

(2) Results with a series of liquids run on different days do not always agree satisfactorily. Hence only curves on the same chart (determined at the same time) may be compared with one another.

(3) When the liquids being tested include some very quickly and some very slowly evaporating solvents, there are decided differences in the temperatures of the liquids after evaporation

has started, although no change is noted in the temperature of the surrounding air. This is, of course, due to the cooling effect of evaporation (*1, 6*) and depends upon the vapor pressure and the latent heat of the liquid. For exact work the temperature of the liquid should be kept constant, although the results obtained by the present method are comparable to those obtained with practical materials, such as lacquers.

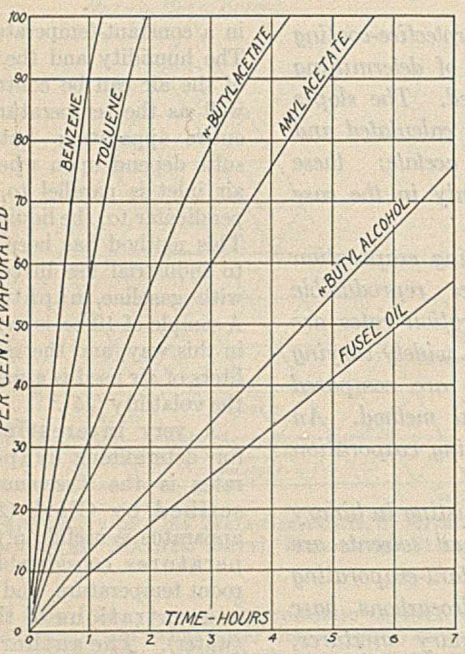

FIGURE 1. TYPICAL EVAPORATION CURVES

(4) The more slowly evaporating liquids are very likely to absorb the vapor of other solvents in the neighborhood, especially where there is a high concentration of vapor. This happens when the evaporations are being conducted in very still air or in a space of limited volume, such as an oven.

(5) Atmospheric humidity is usually thought (*11, 17*) to have very little effect upon the evaporation rates of the usual organic solvents. This is true for solvents which are not miscible with water, such as toluene, butyl acetate, and the like; but, when the solvent is readily miscible with water, the effect of water vapor in the surrounding air is serious (*12*). This is essentially a special form of (2) above.

For exact work the liquids used should be of high purity, and they should be placed in the pans and allowed to come to thermal equilibrium before weighing is started. The weighing should be stopped while there is still some liquid in the pan, in order to avoid the error due to partial wetting of the bottom of the container. The results obtained in this way might be expressed as amount evaporated per square centimeter per hour, instead of as the percentage of sample evaporated. Since it is extremely difficult to work out an absolute method, and since the empirical methods used are so widely different, the best solution seems to lie in the adoption of a standard liquid for comparison. Normal butyl acetate has been suggested for this purpose (*17*), and, since it is very widely used in the industry and its properties are well known, the choice seems to be a wise one.

The author has calculated the slopes of a large number of evaporation curves in order to obtain data concerning the relative evaporation rates of solvents. These values, which are given in Table II, are taken from published work (*3, 5, 7, 10, 14, 16, 17*) and from a large number of unpublished evaporation curves determined by the author at various times. The slopes are all compared with *n*-butyl acetate, to which the arbitrary value of 100 has been assigned. Values of more than 100 indicate faster, and under 100, slower rates of evaporation than that of butyl acetate. The figures have been compiled without regard for temperature or other uncontrolled conditions. In cases where three or more values are available, and especially with the more slowly evaporating solvents, it will be seen that the agreement is fairly good. The most erratic data are those for the quickly evaporating solvents, and it is obvious that much more work along this line would be desirable.

TABLE II. RELATIVE EVAPORATION RATES OF COMMERCIAL MATERIALS

(*n*-Butyl acetate = 100)

SOLVENT	EVAPORATION RATE[a]	AVERAGE
Acetone	1365	1365
Methyl acetate	1125	1125
Chloroform	1045	1045
Ethylene dichloride	638	638
Ethylene acetate	248, 510, 517	425
Ethyl alcohol (95%)	182, 216, 285, 320	251
Isopropyl alcohol (91%)	285	285
1,4-Dioxane	242	242
sec-Butyl acetate	208	208
Toluene	186, 134	160
Isopropyl acetate	159	159
sec-Butyl alcohol	128	128
Diethyl carbonate	110	110
Mesityl oxide	104	104
Diethyl ether of ethylene glycol	100, 75.5, 125	100
sec-Amyl acetate	92	92
Xylene (135–140° C.)	86, 75, 76	79
Butyl propionate	56.3, 53, 68.4, 71.5, 68.5, 60, 63	61
Pentacetate	68.3, 53, 64.5, 61.5	59
Methyl cellosolve	54.8, 47, 71, 55.8, 55	56.7
Turpentine	47.5	47.5
n-Butyl alcohol	56.5, 41, 42.5, 40.3, 43.5	44.7
sec-Amyl alcohol	43	43
sec-Hexyl acetate	41	41
Cellosolve	39, 40.8, 46.8, 32.5, 39	39.8
Butyl butyrate	37.5	37.5
Fusel oil	35	35
Methyl cellosolve acetate	32.6, 33.4, 36.3	34.1
Cellosolve acetate	22.1, 23.6, 30.6, 23.3, 24.2	24.9
Ethyl lactate	22.5, 21.7	22.1
Butyl cellosolve	10, 5.7	8

[a] Evaporation rate = tan of angle the curve makes with the horizontal divided by tan of angle of curve for *n*-butyl acetate × 100.

The data of Table III were obtained in order to check the rates given in Table II. The liquids, which were of good commercial quality (but not especially purified), were placed in aluminum dishes of uniform size and shape and allowed to stand for about 1 hour before being weighed. The dishes were placed on a laboratory bench and protected

TABLE III. EVAPORATION DATA

(Temperature of still air, 18.6–19.8° C.)

SOLVENT	LOSS IN WEIGHT BY HOURS						GRAM/SQ. CM./HOUR	RATE		v. p. × M. W.[a] / 11
	1st	2nd	3rd	4th	5th	Av.				
	Grams	*Grams*	*Grams*	*Grams*	*Grams*	*Grams*				
Acetone	5.07	4.79	4.63	4.16	4.33	4.60	0.1195	980[b]	1365[c]	975
Ethyl acetate	2.80	2.83	2.82	2.60	2.74	2.80	0.0727	590	425	582
Ethyl alcohol	1.35	1.45	1.47	1.43	1.62	1.45	0.0376	308	251	183
Toluene	1.13	1.27	1.26	1.19	1.39	1.25	0.0325	266	160	186
sec-Butyl acetate	0.75	0.81	0.81	0.81	0.97	0.81	0.0210	172	208	180
n-Butyl acetate	0.40	0.47	0.47	0.45	0.56	0.47	0.0122	100	100	100
sec-Amyl acetate	0.40	0.44	0.45	0.46	0.48	0.45	0.0117	96	92	85
Xylene	0.34	0.38	0.39	0.39	0.45	0.39	0.0101	83	79	62
Cellosolve	0.21	0.23	0.23	0.25	0.28	0.24	0.0063	51.5	39.8	37.6
n-Butyl alcohol	0.15	0.18	0.18	0.18	0.21	0.18	0.0047	38.5	44.7	31.7

[a] Vapor pressure times molecular weight, divided by 11.
[b] *n*-Butyl acetate = 100.
[c] According to Table II.

from draft on two sides. They were then weighed (to ±0.005 gram) every hour for 5 hours, during which time the surrounding temperature varied from 18.6° to 19.8° C. The dishes were 7.0 cm. in diameter, thus giving a liquid surface of 38.5 sq. cm. About 25–30 cc. of liquid were placed in each pan.

A comparison of the evaporation rates obtained in this experiment with the average rates of Table II indicates again the uncertainty and erratic nature of determinations of this kind, especially when ordinary commercial liquids are used, and when all the variables are not under control. In this connection the temperatures of the evaporating liquids are shown in Table IV.

TABLE IV. TEMPERATURES OF EVAPORATING LIQUIDS

	AT 18.6° C.[a]	AT 19.8° C.[a]
	° *C.*	° *C.*
Acetone	15.3	16.5
Ethyl acetate	16.7	17.8
Ethyl alcohol	16.8	17.6
Toluene	17.6	18.7
Butyl alcohol	17.9	....
n-Butyl acetate	17.8	....
Xylene	18.0	....
sec-Butyl acetate	17.9	....
Cellosolve acetate	17.8	....
Cellosolve	18.2	....
sec-Amyl acetate	18.1	....

[a] Air temperature.

De Heen (*4*) found in a number of experiments that the quantity of liquid evaporated was proportional to the product of the vapor pressure and the molecular weight, and obtained the figures given in Table V for the liquids indicated.

TABLE V. EVAPORATION RATES (*4*)

LIQUID	QUANTITY OBSERVED	$\frac{v.\,p. \times M.\,W.}{100}$
Water	3.4	3.12
Chloroform	178	191.79
Acetic acid	11	11.34
Ethyl alcohol	23.2	20.24
Ethyl bromide	423	421.05
Carbon disulfide	245	226.48
Ethyl ether	390	320.42

Following this idea, the values for *v. p.* × *M. W.* ÷ 11 are given in the last column of Table III. It will be seen that these values are in the same order as the evaporation rates and of approximately the same order of magnitude. The proportionality factor will depend upon the conditions of the experiment.

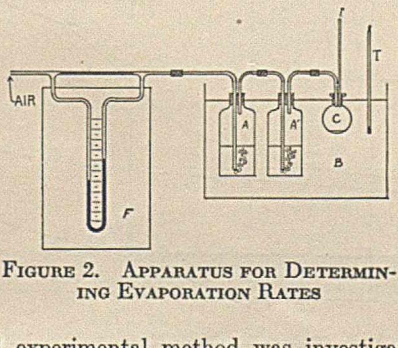

FIGURE 2. APPARATUS FOR DETERMINING EVAPORATION RATES

A second experimental method was investigated, which was similar to that used by several previous investigators and was a modification of that of Polcich and Fritz (*15*). In such an apparatus it is possible to control the temperature of the liquid, the temperature, humidity and velocity of the air, etc., and thus obtain more concordant results. A diagram of the apparatus used is shown in Figure 2. *F* is a flowmeter, reading in liters per minute; *A* and *A'* are wash bottles containing concentrated sulfuric acid; *C* is a short-neck R. B. flask of 200 cc. capacity; *B* is the water bath, kept at ±0.1° C.; and *T* is the thermometer. The air was dry and at the same temperature as the liquid. Unless otherwise noted, all tests were made at 25.0° C. In all the experiments recorded in this paper, air was passed through the apparatus at the rate of 1.00 liter per minute. The completion of evaporation was noted visually and could be ascertained within 30 seconds. Only pure liquids having no slowly evaporating residue were used.

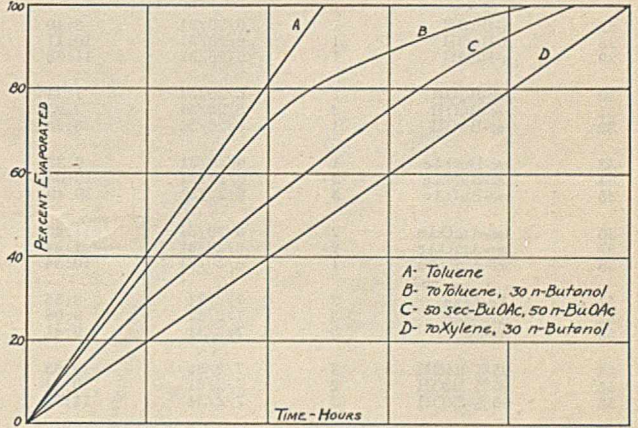

FIGURE 3. EVAPORATION CURVES OF FOUR TYPES OF SOLVENTS

In order to standardize the apparatus, *n*-butyl acetate was first studied, and runs were made with 1.0, 2.0, and 3.0 cc. of liquid in the flask, *C*. The liquid was measured into the flask with a graduated capillary pipet, and the flow of air was adjusted to the proper rate before inserting the stopper into the flask containing the liquid.

Since no attempt was made to maintain a constant area of evaporating liquid, it was necessary to standardize the apparatus for each volume of solvent used. The results obtained with *n*-butyl acetate are given in Table VI.

TABLE VI. EVAPORATION OF *n*-BUTYL ACETATE AT 25.0° C.

EXPT.	VOL. USED	TIME OF EXPERIMENT Date	Started	Dry	Total	REMARKS
	Cc.				*Min.*	
3	1	6/16/31	9:15	9:56	41	Rain, very humid, room temp. 24–25° C.
4	1	6/16/31	10:00	10:41	41	
8	1	6/20/31	10:18	10:57	39	Hot, room temp. 29–31° C.
9	1	6/20/31	11:00	11:40	40	
15	1	6/24/31	3:50	4:28	38	Clear, room temp. 24–26° C.
16	1	6/30/31	11:53	12:35	42	Hot, room temp. 29–31° C.
Av.	1	..	..	..	40	....
1	2	6/13/31	9:10	10:22	72	Clear, room temp. 24–25° C.
2	2	6/13/31	10:25	11:39	74	
5	2	6/16/31	11:21	12:30	69	Rain, very humid, room temp. 24–25° C.
6	2	6/16/31	12:33	1:41	68	
7	2	6/16/31	1:48	2:56	68	
13	2	6/24/31	1:31	2:37	66	Clear, room temp. 24–26° C.
14	2	6/24/31	2:40	3:47	67	
Av.	2	..	..	..	69	....
10	3	6/24/31	8:48	10:19	91	Clear, room temp. 24–26° C.
11	3	6/24/31	10:21	11:51	90	
12	3	6/24/31	11:54	1:27	93	
Av.	3	..	..	..	91	

Further runs were then made with other purified solvents to obtain their evaporation rates compared with *n*-butyl acetate. These data are given in Table VII. A summary of the evaporation rates obtained by the various methods is given in Table VIII. On account of the greater accuracy, the author favors this method, using the apparatus of Figure 2.

TABLE VII. EVAPORATION RATES OF VARIOUS SOLVENTS

(n-Butyl acetate = 100, temperature = 25.0° C.)

			Time of Experiment					
Expt.	Solvent	Vol. Used Cc.	Date	Started	Dry	Time Min.	Rate[a]	Remarks
20	Toluene	2	6/25/31	8:35	9:13	38	181	Room temp. 25-26° C.
21	Toluene	2	6/25/31	9:15	9:51½	36½	189	
22	Toluene	3	6/25/31	9:53	10:42½	49½	184	
23	Toluene	3	6/25/31	10:45	11:33	48	189	
							Av. 186	
24	Xylene (5°)	2	6/25/31	12:47	2:35	108	64	....
25	Xylene	1	6/25/31	2:37	3:37	60	66.6	
26	Xylene	1	6/25/31	3:39	4:40	61	65.5	
							Av. 65.5	
27	n-BuOH	1	6/26/31	8:40	10:09	89	45	Room temp. 26-28° C.
28	n-BuOH	1	6/26/31	10:11	11:35	84	47.6	
29	n-BuOH	1	6/26/31	11:38	1:08	90	44.5	
							Av. 45.7	
30	*sec*-BuOH	2	6/26/31	1:11	2:16	65	106	....
31	*sec*-BuOH	2	6/26/31	2:23	3:24	61	113	
32	*sec*-BuOH	1	6/26/31	3:28½	4:05	36½	110	
							Av. 110	
33	*sec*-BuOAc	1	6/29/31	9:37	10:02	25	160	Hot, room temp. 29-31° C
34	*sec*-BuOAc	2	6/29/31	10:04	10:47	43	160	
35	*sec*-BuOAc	3	6/29/31	10:49	11:44	55	165	
							Av. 162	
36	*sec*-AmOAc	2	6/29/31	11:48	1:22	94	73.5	Hot, room temp. 29-31° C
37	*sec*-AmOAc	2	6/29/31	1:34	3:12	98	70.5	
38	*sec*-AmOAc	1	6/30/31	10:54	11:49	55	74.5	
							Av. 73	
51	Acetone	3	7/2/31	8:55	9:05½	10½	865	Room temp. 25-26.5° C.
52	Acetone	3	7/2/31	9:08	9:19	11	828	
53	Acetone	3	7/2/31	9:41	9:51½	10½	865	
							Av. 850	
54	95% EtOH	3	7/2/31	9:55	10:42½	47½	192	....
55	95% EtOH	2	7/2/31	10:44	11:19½	35½	194	
56	95% EtOH	2	7/2/31	11:23	11:58½	35½	194	
							Av. 193	
57	Cellosolve	1	7/2/31	12:05	1:56	111	36	....
58	Cellosolve	1	7/2/31	2:00	3:45	105	38	
							Av. 37	
60	85% EtOAc	3	7/3/31	8:32	8:51	19	480	Humid, room temp. 26° C
61	85% EtOAc	3	7/3/31	8:52½	9:11	18½	492	
62	85% EtOAc	3	7/3/31	9:14	9:33	19	480	
							Av. 485	

[a] Time for evaporation of n-BuOAc ÷ time for evaporation of other liquid.

TABLE VIII. SUMMARY OF EVAPORATION RATES

	Rate			$\frac{v.p. \times M.W.}{11}$
	Table II	Table III	Table VII	
Acetone	1365	980	850	975
Ethyl acetate	425	590	485	582
95 per cent ethyl alcohol	251	308	193	183
Toluene	160	266	186	186
Xylene	79	83	65.5	62
sec-Butyl acetate	208	172	162	180
n-Butyl acetate	100	100	100	100
sec-Amyl acetate	92	96	73	85
n-Butyl alcohol	44.7	38.5	45.7	31.7
sec-Butyl alcohol	128	....	110	87.5
Cellosolve	39.8	51.5	37	37.6

EVAPORATION OF LIQUID MIXTURES

BINARY MIXTURES. The phenomena connected with the evaporation of a mixture of two liquids are very similar to those concerning the distillation of a mixture, but are not identical. The two kinds of mixtures to be considered are: so-called ideal mixtures; and those which exhibit a maximum vapor pressure, i. e., constant-evaporating mixtures. (The author has not encountered any cases of minimum vapor-pressure mixtures at ordinary temperatures.)

The first group includes mixtures containing: members of the same homologous series, such as ethyl and butyl acetates, toluene and xylene, etc.; or two compounds of a similar nature, such as a hydrocarbon and a halogenated hydrocarbon, a hydrocarbon and an ester (except lower members), an aliphatic and an aromatic hydrocarbon, etc. In cases of this kind, both solvents evaporate simultaneously at different rates and have no effect upon each other. When the faster-evaporating component is gone, the remainder of the other component evaporates at a constant rate. The evaporation graph of such a mixture is usually curved very much as shown at *C* in Figure 3.

The constant-evaporating mixtures occur in mixtures of two dissimilar compounds, such as an alcohol and a hydrocarbon, and in general with the same compounds that form constant-boiling mixtures at higher temperatures. The composition of the constant-evaporating mixture is always different from that of the constant-boiling mixture, because dp/dt is almost always different for the two components. A number of constant-evaporating mixtures occur between the alcohols and the hydrocarbons commonly used in lacquer solvents. The author and Reid (*10*) have previously alluded to these, but their compositions were not determined.

King and Smedley (*13*) have described a very simple method of locating the constant-evaporating mixture of two compounds by means of refractive index readings, taken on an Abbé refractometer, and have located the mixture of carbon tetrachloride and ethyl alcohol which evaporates at a constant rate. (These mixtures evaporate faster than either component alone.) A few data on mixtures of maximum vapor pressure are also given in International Critical Tables (*11*). The author has determined the approximate

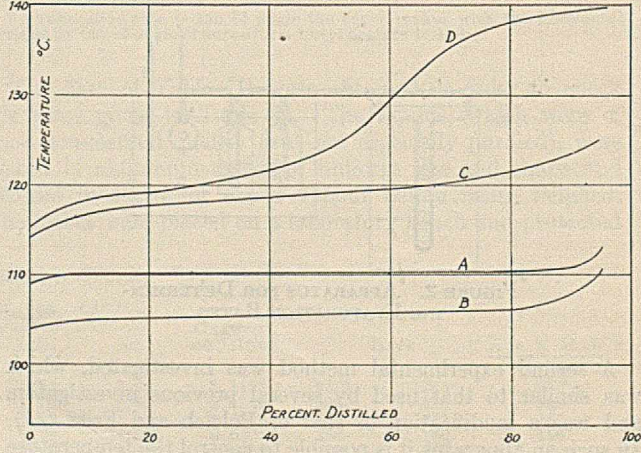

FIGURE 4. DISTILLATION CURVES OF LIQUIDS OF FIGURE 3

compositions of several new constant-evaporating binary mixtures, using the method of King and Smedley. The results are shown in Table IX.

TABLE IX. CONSTANT-EVAPORATING MIXTURES

(Temperature = 20–25° C.)

COMPOSITION *% by vol.*	REFERENCE
Benzene, 47; ethyl acetate, 53	(*11*)
Benzene, 69; methanol, 31	(*11*)
CCl_4, 82.6; ethyl alcohol, 17.4	(*13*)
CCl_4, 70; methyl ethyl ketone, 30	...
Toluene, 45; 95% ethyl alcohol, 55[a]	...
Toluene, 48; 98% isopropyl alcohol, 52[a]	...
Toluene, 78; *sec*-butyl alcohol, 22	...
Toluene, 92; *sec*-amyl alcohol, 8	...
Xylene, 35; *sec*-butyl alcohol, 65	...
Xylene, 65; *sec*-amyl alcohol, 35	...
Xylene, 70; *n*-butyl alcohol, 30	(*10*)
Xylene, 80; fusel oil, 20	...
Xylene, 83; cellosolve, 17	...

[a] For practical purposes, these are considered binary mixtures, the water present in the alcohols being neglected.

Such mixtures as these are interesting from the standpoint of the possibilities they offer in connection with the formulation of solvent mixtures for various purposes. The fact that they also form constant-boiling mixtures when distilled should be borne in mind when examining such solvent mixtures by fractional distillation.

An interesting comparison of evaporation curves (percentage evaporated *vs.* time, determined by the usual method) and distillation curves for the same solvent mixtures is given in Figures 3 and 4. These two types of curve may be considered analogous to the pressure-volume and temperature-entropy diagrams of thermodynamics. A mixture or solvent which gives a straight line on one diagram may or may not give a straight line on the other. There are four possibilities, an example of each being shown:

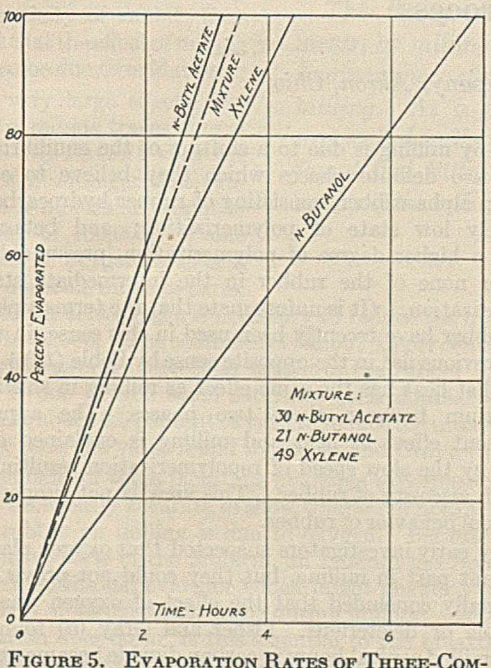

FIGURE 5. EVAPORATION RATES OF THREE-COMPONENT MIXTURE AND ITS COMPONENTS

A. Straight evaporation curve and straight (flat) distillation curve, possible only with pure compounds.

B. Curved evaporation curve and flat distillation curve, constant-boiling mixtures.

C. Curved evaporation and curved distillation curves, so-called ideal mixtures of similar compounds.

D. Straight evaporation curve and curved distillation curve, constant-evaporating mixtures.

The diagrams emphasize the fact that evaporation characteristics cannot be accurately predicted from distillation data. For example, compare curves *A* and *B* in both diagrams.

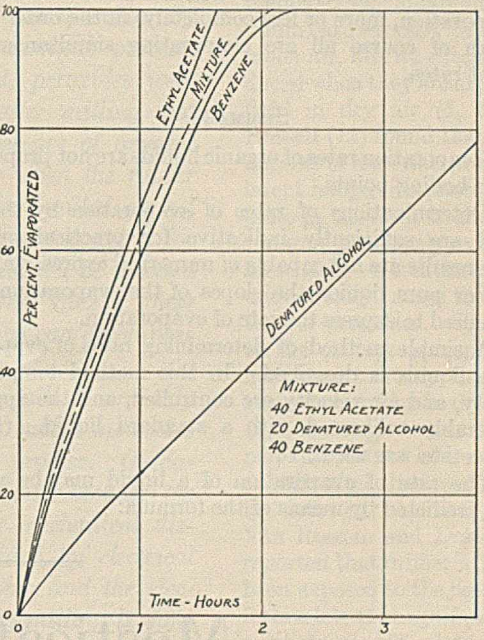

FIGURE 6. EVAPORATION RATES OF THREE-COMPONENT MIXTURE AND ITS COMPONENTS

TERNARY MIXTURES. The investigation of three-component mixtures as a class is much more difficult than the study of binary mixtures. The principal stumbling block is the lack of suitable analytical methods for determining the composition of such mixtures. Furthermore, ternary azeotropes (either at the boiling point or at room temperature) are of rare occurrence, especially in mixtures of solvents encountered in connection with lacquers, etc. Water is frequently a component of such mixtures, and, since the presence of sufficient quantities of water in a lacquer is fortuitous, ternary constant-evaporating mixtures are not of particular importance in this connection.

The author has investigated one three-component mixture which, while not a true constant-evaporating mixture, nevertheless evaporates at a uniform rate without substantial change in composition. In comparing the binary constant-evaporation mixture of xylene and butyl alcohol with other compounds, such as the esters, it was found that the evaporation curve of this mixture was almost identical with that of butyl acetate. Hence a mixture was made of butyl acetate with xylene and butyl alcohol in the ratio of 70:30, which had the following composition:

	%
n-Butyl acetate, by weight	30
n-Butyl alcohol	21
Xylene	49
	100

Upon examination, it was found that this mixture evaporated at a uniform rate, as shown in Figure 5. Four hundred grams were then evaporated at room temperature until only 20 grams (5 per cent) remained. From determination of the acetyl and saponification values, and comparison with those of the original mixture, it was found that the change in the amounts of the various ingredients was not over ±5 per cent. Another mixture, similar to the above, is shown in Figure 6.

Other three-component mixtures, infinite in number, are possible with the various solvents now available, but it is probable that few, if any, are true constant-evaporating mixtures. The behavior of a mixture of benzene, butyl acetate, and amyl alcohol has been referred to by Hofmann and Reid (*9*). The ingredients are removed from the mixture by evaporation, more or less completely, in the order named, although of course all are evaporating simultaneously at different rates.

SUMMARY

1. Evaporation rates of organic liquids are not proportional to their boiling points.
2. Determinations of rates of evaporation by the usual method are sufficiently indicative for practical purposes, but the results are not capable of numerical expression.
3. For pure liquids the slopes of the evaporation curves may be used to express the rate of evaporation.
4. A simple method of determining rates of evaporation of pure liquids is described. In this method temperature, humidity, and air velocity are controlled, and the apparatus is preferably calibrated with a standard liquid. (Normal butyl acetate was used.)
5. The rate of evaporation of a liquid may be approximately predicted by means of the formula:

$$\text{vapor pressure} \times \text{mol. wt.} \div 11$$

which gives a rate of 100 for *n*-butyl acetate (20° C.).

6. The compositions of several new binary constant-evaporating mixtures and of two ternary mixtures which may be called "apparent constant-evaporating mixtures," have been determined.

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Mastication of Rubber

An Oxidation Process

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THE mechanism of the breakdown of rubber on the mill has been investigated by many workers, and many different theories have been advanced to explain the changes which occur. In some cases the theories have been based on a postulated structure of the latex particle, but, more often, they were *ad hoc* explanations based on the authors' pictures of the structure of the rubber molecule. Countless attempts have been made to distinguish between "depolymerization" and "disaggregation" of rubber molecules, where in many cases the difference is merely one of definition. Only recently have data become available to show that milling is not the simple mechanical process it once was thought to be, but is essentially a chemical reaction.

PREVIOUS WORK

It is well known that the latex globules are broken up during milling (*8, 9, 10*), and Van Rossem (*27*), adopting Hauser's picture of the latex particle, claimed that the plasticizing effect of milling is due to the mixing of the soft inner phase with the hard outer phase of the globules. This does not explain why the plasticity of rubber continues to increase during milling, even when all the latex globules are broken up, nor does it agree with the results of Staudinger (*23*), which indicate that the molecular weight of milled rubber is considerably less than that of unmilled. Staudinger believes that the breakdown of rubber on the mill is a mechanical disruption of the primary valence bonds in the rubber molecules, such as occurs in crushing a diamond. Pummerer (*17*), on the other hand, claims that the molecular weight of rubber is low, and milling merely breaks up the micelles, which are large aggregates of molecules.

Bary and Hauser (*1*) have claimed that the softening of rubber by milling is due to a shifting of the equilibrium between two definite phases which they believe to exist in rubber; alpha-rubber, consisting of rubber hydrocarbon in a relatively low state of polymerization; and beta-rubber, having a higher degree of polymerization, presumably with little or none of the rubber in the intermediate states of polymerization. (It is unfortunate that the terms alpha- and beta-rubber have recently been used in this sense, in view of their previous use in the opposite sense by Pohle (*16*).) They claim that heat has the same effect as milling in shifting the equilibrium between these two phases. The apparently permanent effect of heat and milling is explained on this theory by the slow speed of repolymerization resulting from the high viscosity of rubber. This view is not supported by the actual behavior of rubber.

Many early investigators suspected that oxygen played an important part in milling, but they could not prove it, and they finally concluded that the effect of oxygen was either negligible or deleterious. Fisher and Gray (*6*) found that rubber milled several hours in carbon dioxide became very soft and tacky, but the change in unsaturation could not be measured (i. e., was less than 0.5 per cent). Rubber milled several hours in air had its unsaturation lowered by about 2 per cent, which, they said, may have been due to oxidation or to the formation of a cyclo-rubber. Garner (*8*) claimed that milling first depolymerized or disaggregated the rubber hydrocarbon, after which it could react with oxygen to become tacky. Messenger (*14*) found that milling rubber changed its heat of combustion by less than 0.5 per cent, although the viscosity was changed by a factor of 20, which seemed to indicate the amount of oxidation which occurs during milling is negligible.

CHANGES IN RUBBER which occur during mastication have been studied in an attempt to determine whether the breaking down of rubber by milling is a mechanical or a chemical process. Using the photographic-plate test, peroxides were detected in smoked sheets, both after milling and after exposure to light in the presence of oxygen, and the concentration was higher when the rubber was milled on cool rolls than when milled on hot rolls. Pale crepe did not give as strong a test for peroxides, while the peroxides could not be detected at all in fine Para and sprayed latex. These rubbers contain some material which can decompose hydrogen peroxide.

The softening of rubber on the mill is probably due to the breaking up of the long rubber molecules into shorter ones by an oxidation process. Oxidation occurs quite rapidly on the mill because the rubber molecules are activated by mechanical distortion, and the oxygen is activated by electrical charges. The stresses in the rubber and the electrical charges are both greater when milling is done on cool rolls than when done on hot rolls, which accounts for the greater effectiveness of cold-milling.

This theory was verified by the peroxide experiments, by milling peroxides into rubber, and by the luminescence effects which were observed during milling. As a final check on the theory, rubber was milled in the presence of various gases. It was found that little, if any, breakdown of the rubber occurs if the milling is done in the absence of oxygen.

The view was further supported by the fact that rubber could be softened to some extent by heating in steam or carbon dioxide (*9*, *15*), while heating for a long time in air totally ruined the rubber. The belief in the deleterious effect of oxygen led the Dunlop Rubber Company (*31*) to patent the method of softening rubber by heating it in an inert non-oxidizing atmosphere previous to milling. Staudinger (*22*) also patented the method of masticating rubber in an inert atmosphere to avoid the deleterious effects of oxygen.

Recently Fry and Porritt (*7*) showed that nearly all the permanent softening, which occurs in heating rubber in a supposedly inert atmosphere, actually is due to the traces of oxygen which are present, even 0.01 per cent of oxygen causing a very marked effect on rubber when it is heated for several hours at 150° C. From the similarity in the effects of heating and milling on the viscosity and plasticity of rubber, they suggest that the effect of milling may also be due to oxidation.

The very large effects produced by minute traces of oxygen are consistent with the views of Staudinger that rubber has a molecular weight of the order of 100,000. If one molecule of oxygen breaks a rubber molecule into two parts, only 0.03 per cent oxygen is necessary to reduce the molecular weight to 50,000. The combining of about 0.5 per cent oxygen reduces the average molecular weight of the rubber to about 5000. If one oxygen atom saturates each double bond, it takes only about 0.5 per cent oxygen to reduce the unsaturation by 2 per cent, the value found by Fisher and Gray.

In the light of these facts, the available experimental data are not sufficiently accurate to show whether or not the softening of rubber on milling is due to oxygen. Because of the inconclusive state of the problem, an attempt has been made to obtain additional evidence which might answer two questions: first, does oxidation occur during milling; and second, if oxidation does occur, is this essential to the breakdown of the rubber on the mill? In the first part of this work, several different lines of indirect evidence were obtained to throw light on these questions. The conclusions from the early work were then verified by milling rubber in the presence of various gases. The results of this work are in agreement with those of a similar test recently reported by Cotton (*2*).

If rubber is oxidized during milling, the first product formed probably is a peroxide, since most unsaturated compounds are oxidized through the formation of intermediate peroxides. One of the most sensitive, though unfortunately not a specific test for volatile peroxides, is the formation of latent images when they act on photographic plates (*13*). The action of hydrogen peroxide on a plate is similar in every respect to that of light (*21*). It is reported that the test is so sensitive that it can detect the peroxides formed when certain metals (zinc, aluminum, cadmium) are exposed to light in moist air, but no effect is produced when they are exposed to light in dry air (*5*, *13*, *19*). Russell (*18*) found that a large number of materials produced a latent image on a photographic plate in the dark if the material were previously exposed in air to light—a treatment which undoubtedly causes the formation of peroxides. This effect on the photographic plate has been used to study the formation of peroxides in drying oils (*24*), although the amounts of peroxide formed here are great enough after short exposure to be detected chemically (*25*). Van Rossem and Dekker (*28*) reported that rubber which had been exposed to the light could form a latent image if placed on a photographic plate in the dark, and they found the effect to be greater with smoked sheets than with pale crepe.

If peroxides are formed during milling, they might be detectable by this method. Negative results, of course, would be inconclusive, since, even though peroxides were formed during milling, they might not be volatile, or the surface concentration might not be great enough, or catalysts might be present which would destroy the peroxides before they could be detected. The following experiments show that peroxides are formed in rubber during milling just as on exposure to the light, but that they can be detected only in certain rubbers. Some rubbers contain catalysts which decompose peroxides, and these rubbers also exhibit the slowest plasticity changes during milling.

FORMATION OF PEROXIDES IN RUBBER

EFFECT OF LIGHT. Samples of rubber were exposed for various times to a 220-volt printing arc, using National Carbon Company's Therapeutic "A" carbons, usually at a distance of 50 cm. from the arc. In every case a part of the sample was protected from the light by a strip of metal foil, leaving a control area of unexposed rubber on each sample. After exposure, the strips of metal were removed, and the exposed side of the rubber samples put directly on the emulsion of a photographic plate where they usually were allowed to remain in the dark for about 18 to 24 hours, after which the plate was developed.

The first attempts to duplicate the work of Van Rossem and Dekker failed, because ordinary process or panchromatic plates were used. When Eastman "Speedway" or Gavaert "Super Sensima" plates were used, however, samples of smoked sheet produced a very strong image after less than a

1-minute exposure to the arc, and these plates were used in all subsequent work. It is known that the sensitivity of different plates to hydrogen peroxide varies enormously just as does their sensitivity to light (*30*).

To show that the formation of the latent image was due to oxygen, the following experiment was performed:

> Strips of crude smoked sheet were placed in Pyrex test tubes, through which air, carbon dioxide, and hydrogen, respectively, were allowed to flow for about 6 hours. Another test tube containing a strip of smoked sheet was evacuated to a pressure of 3.10^{-4} mm. of mercury for the same time, giving the air present in the sample a chance to diffuse out. The evacuated test tube was then sealed off, and the others were closed with clamps to exclude the air. The hydrogen and carbon dioxide, which were taken directly from commercial supply tanks, undoubtedly contained traces of oxygen as an impurity. Two of the tubes were filled with hydrogen and from one the stopper was partially removed for a fraction of a second to admit a small amount of air. The samples were given a relatively long exposure (10 minutes) to the arc light while surrounded by these gases, and another sample of smoked sheet was exposed directly to the light without being shielded by glass.

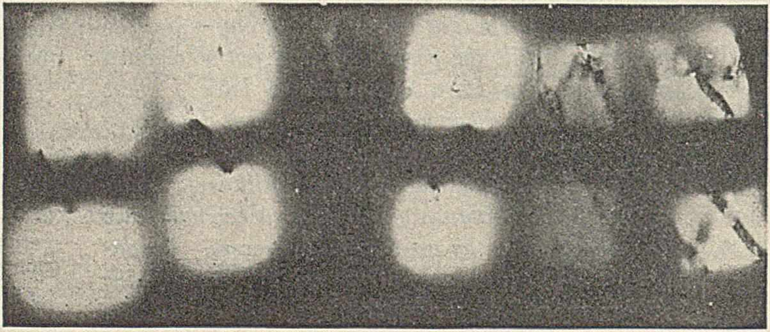

Figure 1. Images Formed by Smoked Sheet When Exposed to Arc Light in Different Gases

(All except No. 1 exposed in Pyrex test tubes)

1. Air
2. Air
3. Vacuum (3.10^{-4} mm. Hg)
4. Hydrogen containing air
5. Hydrogen
6. Carbon dioxide

The results are shown in Figure 1. It is seen that the sample exposed in the evacuated tube produced only a barely detectable image. The samples exposed in hydrogen and carbon dioxide formed considerably stronger images, though they were still much weaker than the image formed by the sample exposed in contact with an appreciable amount of air. The dark band across each sample shows where the rubber was protected from the light by the metal strip. It is difficult to say whether the images formed after exposure in hydrogen and carbon dioxide are due to oxygen present as an impurity in the gas or to oxygen originally present in the sample, although the former is more probable. The results show that extreme ultra-violet light is not necessary to produce this effect, since the activating rays passed through the glass.

The formation of the latent image is not due to a luminescence or phosphorescence of the rubber, since no image is formed if the rubber is separated from the photographic emulsion by a microscope cover-glass, or even a thin (0.0010-inch) sheet of cellophane, but the active material can travel through a few millimeters of air and still affect the plate. This material is undoubtedly a volatile peroxide, possibly hydrogen peroxide which splits off from the oxidized rubber. In the rest of the report this volatile material will be referred to as hydrogen peroxide.

Effect of Milling. To determine if milling would also produce this peroxide in smoked sheet, one sample was milled 4 minutes on a cold 4 × 4 inch mill, while another was milled the same length of time with steam-heated rolls. A third sample was dead-milled and then allowed to stand 3 days before being put on the photographic plate. Other samples of crude smoked sheet were exposed to light and then were placed with the milled samples on the photographic plate.

The results, shown in Figure 2, indicate that not only is the peroxide formed during milling, but that its effective concentration is higher after cold-milling (sample 2) than after hot-milling (sample 3), and that some of the peroxide remains in the rubber for at least 3 days after milling (sample 4).

The difference in the results after hot- and cold-milling may be attributed to the fact that cold-milling is more effective than hot-milling in forming the peroxide, and to a more rapid decomposition of the peroxide at high temperatures. The evidence that the formation of the peroxide is more rapid at the lower temperature suggests that this phenomenon is fundamentally related to the breakdown of the rubber.

The stability of the peroxide was tested by storing samples treated the same as those in Figure 2 for 18 days, and then putting them on a photographic plate. The samples which were milled cold or exposed to light for long periods still produced faint but definite images after this time. It is possible that none of the original peroxide formed by the light or milling remained after 18 days, but that the decomposition of the original peroxide started reaction chains, resulting in the formation of more rubber peroxide.

Heating a sample of smoked sheet for 5 minutes at 200° C. in unpurified carbon dioxide, after it had been exposed to the light, weakened but did not destroy its ability to affect a photographic plate; after heating for 15 minutes under these conditions, the rubber still had a slight but definite effect on a plate. Heating smoked sheet in air at this temperature caused it to become so tacky that it could scarcely be removed from photographic plate after resting on it overnight. There was some evidence, however, of the formation of a very weak latent image.

Results with Different Rubbers. The formation of peroxide by light and milling was studied for several different rubbers. It was found that they produced images of widely different intensities, but it was particularly noted that the order of intensity for different rubbers was always the same, whether the peroxide was formed by exposure to light or by milling. Smoked sheet and balata formed the strongest images, while pale crepe always produced a considerably weaker image, and none at all was obtained from No. 1 sprayed latex, fine Para, or guayule. That the rate of change of plasticity with time of milling for different rubbers increases in the order—sprayed latex, pale crepe, smoked sheet (*4*)—seems to signify that the peroxide formation and change in plasticity are quantitatively related.

The negative results for sprayed latex and fine Para probably are not due to any lack of formation of peroxide, but to the fact that the peroxide is decomposed by some material present in these rubbers soon after it is formed. This is shown by the fact that a 50:50, or even in some cases a 25:75, mixture of sprayed latex and smoked sheets will not produce any latent image after being milled or exposed to light, or after both treatments.

This view was confirmed by tests in which hydrogen peroxide was milled into sprayed latex, Para, and smoked sheet. When the samples were put on a photographic plate within an hour after milling, each of them formed a very strong image. However, if the batches were allowed to stand for 24 hours, and the samples then put on photographic plates, the image formed by smoked sheet was almost as strong as before; but the sprayed latex and Para formed no image, showing that during this period they had decomposed the peroxide which had been added.

Several unsuccessful attempts were made to remove from the rubber the material that destroyed the peroxide. Soaking thin strips of sprayed latex in running warm water, in acetone, or in alcohol for periods up to 11 days, followed by drying for about 8 hours, was not effective; nor did drying a sample over sulfuric acid for 11 days before exposing to light render it active toward a photographic plate. Smoked sheet was not affected by drying, but soaking it in acetone or alcohol for 11 days greatly reduced its power to form a latent image after exposure to the light. After soaking the smoked sheet in water for 11 days and drying in air for 8 hours, it did not have the power to form a latent image, though the soaking in water caused the sample to become very tacky.

An uncured smoked sheet–sulfur mixture produced an image after exposure to the light, but with progressively longer cures the ability to form a latent image was gradually reduced, and the fully cured and overcured samples did not form an image under any conditions. This may have been due to the decomposition of the peroxide by traces of hydrogen sulfide formed during cure. It is also possible that vulcanized rubber itself reacts more readily than unvulcanized rubber with the peroxide.

Effect of Various Chemicals. It was thought at one time that this phenomenon might offer a good general method of testing antioxidants. This did not prove to be the case, for most age-resisters, because of their amine content, affected the plate without being exposed to the light. However, several interesting results were obtained in the presence of metal soaps. Stearates of copper, cobalt, manganese, and zinc, and linoleates of copper and cobalt were used, milling 3 per cent of each into smoked sheet.

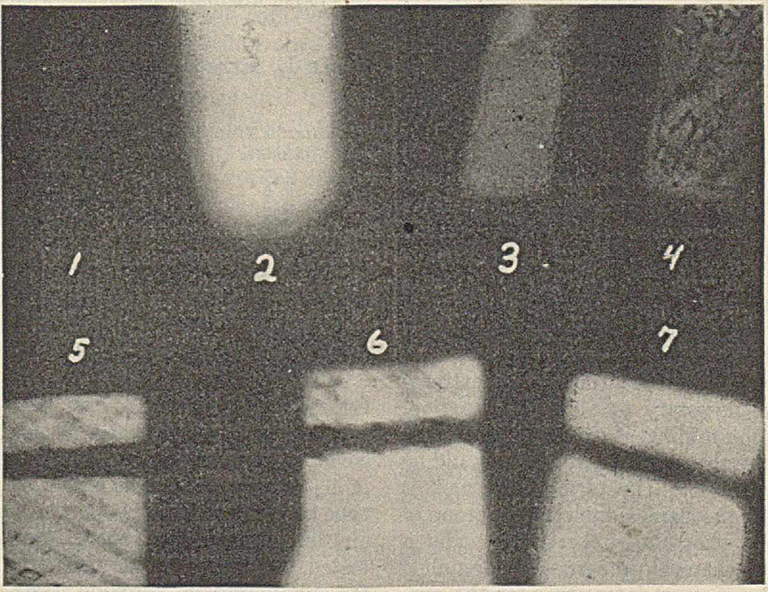

Figure 2. Peroxide Formation by Light and Milling

1. Control (untreated)
2. Milled 4 minutes on cold mill
3. Milled 4 minutes on mill
4. Dead-milled and stored 3 days
5. Exposed to arc light 30 seconds at 25 cm.
6. Exposed to arc light 30 minutes at 25 cm.
7. Exposed to arc light 30 minutes at 60 cm.

When samples of these stocks, and of the controls milled without the addition of any metal soap, were placed on a photographic plate immediately after milling, moderately strong images were formed by the controls and by the stocks containing zinc and manganese stearates, but no images were formed by the stocks containing copper and cobalt soaps. After two or three days the peroxides formed during milling could no longer be detected in any of the stocks. Samples of each stock were then exposed to the arc light and again tested for peroxides. The order of intensity of the images was the same as found immediately after milling. The copper and cobalt soaps destroyed the peroxides formed by the light, so that these stocks produced no images; from the stocks containing zinc and manganese soaps and from the controls, dense images on the photographic plate were obtained. Similar results were obtained after the stocks had stood for various times up to a month, except for the sample containing cobalt linoleate. At the end of a week this sample produced no image on a photographic plate before being exposed to the light, but, after exposing the sample to the arc light for 30 minutes, it formed a very dense image that extended for several centimeters from the sample. The samples containing cobalt stearate and both of the copper soaps produced no image whatsoever after this treatment. Two weeks after the cobalt linoleate was added to the rubber, it had accelerated the oxidation so much that it caused this stock to give a very dense image on the photographic plate, even without exposing the rubber to the light. Neither cobalt stearate nor either of the copper soaps had this effect, even after the samples had stood for a month. Copper linoleate made the rubber very soft and sticky, but this oxidation was not accompanied by an evolution of hydrogen peroxide which could be detected on a photographic plate. There seems to be a fundamental difference in the effects of both copper and cobalt and of the saturated and unsaturated acid soaps in the rubber. It is interesting to compare these results with the effect of metal soaps in linseed oil. The addition of driers (lead, cobalt, and manganese soaps) reduces the amount of hydrogen peroxide given off; the addition of soaps of zinc, cadmium, or aluminum, which are not driers, enormously increases the amount of hydrogen peroxide liberated by the drying oil film (*24*).

Attempts to Develop Chemical Tests for Peroxides. Although it is very improbable that the above results could be due to anything but peroxides, or at least to some form of active oxygen, an attempt was made to obtain confirmatory chemical tests for peroxides. However, these were not successful except in the case of the sample containing copper linoleate which gave off large quantities of hydrogen peroxide. On making an aqueous extract of smoked sheet, or even rinsing the surface of smoked sheets a few times, a solution is obtained which will reduce either ferric chloride or free iodine; thus the usual tests for peroxides, such as the titanium sulfate, chromic acid or starch–potassium iodide tests, are useless to detect the small amounts of peroxides formed by light or milling. There are more water-soluble reducing materials present in smoked sheets than are required to decompose any peroxides that may be present, so that the peroxides are reduced as soon as the surface is wet. This also explains why the sample of smoked sheet soaked in water for 11 days could not form any image on the photographic plate.

A few attempts were made to obtain solutions of the peroxides in various solvents, such as chloroform, carbon tetrachloride, etc., by washing with these solvents the surface of samples that had been milled or had been exposed to light, but in no case was a satisfactory test obtained. No peroxide could be detected in air which flowed past a sample of smoked sheet in a Pyrex test tube during exposure of several hours to the arc light. Undoubtedly with sufficient time and patience a chemical test could be obtained, but this was not considered necessary in view of the evidence later obtained which conclusively showed the importance of oxygen during milling.

MECHANISM OF OXIDATION ON THE MILL

The above experiments show that rubber is oxidized at a fairly rapid rate during milling in air, and they raise the question as to how this oxidation is brought about. Rapid oxidation is probably caused by two factors: the increase in the potential energy of the long rubber molecules, due to mechanical deformation which makes them more reactive; and the activation of the oxygen by the electric charge developed by the rubber.

It is well known that vulcanized rubber is much more reactive to ozone and oxygen when slightly stretched than when unstretched (*11*), and this is also true for unvulcanized rubber. The stretching of rubber causes a distortion of the molecules, increasing their internal energy just as straining increases the single electrode potential of metals and their reactivity toward oxygen (*26*). This factor is probably more effective whenever the molecules are larger, and thus the larger molecules are broken down first.

The rate of oxidation is also increased by the activation of oxygen during milling, owing to the electric charge which develops. It has been shown (*3*) that, in the presence of moisture, oxygen has a strong affinity for electrons, forming ion clusters. Since the rubber acquires a charge on going through the mill, the oxygen probably tends to form ion clusters on the surface of the rubber, which could easily cause the formation of a rubber peroxide.

The charge on the rubber may reach a potential sufficiently high not only to form ion clusters on the surface of the rubber, but also to form ionized oxygen molecules, O_2^- and O_2^+, and even ionized oxygen atoms and ozone. In these cases the oxygen would be even more strongly activated than when it was in the form of ion clusters; and it probably would combine with the strained rubber more readily, although this extreme activation probably is not necessary to cause the reaction. With these conditions during milling, it would be surprising not to have the rubber molecules oxidized, in fact it would be almost impossible to prevent it. The term "molecule" is used here in the sense of the mechanical molecule or group of atoms which stay together when the rubber flows under a shearing stress, since the mechanical properties of the milled rubber are the ones which are most interesting for the purposes of these experiments. This term will be discussed more fully elsewhere. However, the evidence strongly suggests that the chemical and mechanical molecules of rubber are the same.

It does not follow from this theory that antioxidants will necessarily prevent the softening of rubber on the mill, although it would be expected that part of the antioxidants would be oxidized. Overmilled stocks have notoriously bad aging properties (*29*), probably owing to the oxidation of the natural and added age-resisters. It is well known that most of the chemical antioxidants are not effective against sunlight or ozone aging, where rubber is attacked by activated oxygen, and good age-resisters may also be ineffective in preventing the activated rubber from being attacked by activated oxygen on the mill.

CONFIRMATORY EVIDENCE FOR THE PROPOSED THEORY OF MILLING

ELECTRICAL EFFECTS. The importance of the electrical effects in the breakdown of rubber during milling as postulated above is supported by some rather interesting observations on the accompanying luminescence effects. When rubber is milled on a 4 × 4 inch mill with cold rolls, no electrical discharge takes place underneath the bite, as might be expected, but there is a more or less even glow over the surface of the rubber for about 1 or 2 cm. where the rubber enters the bank, and occasionally tiny sparks can be seen jumping from the blanket to the bank. In fact, most of the frying and crackling noise that is heard on a small mill, which is often attributed to the bursting of small air bubbles, is due to these sparks. This effect can be observed with gas-black mixtures as well as with pure gum stocks and with dead-milled, as well as slightly milled rubber, providing the rolls are cold. However, if the rolls are heated, this effect disappears, but it reappears on cooling the rolls. This shows a striking correlation with the smaller yield of peroxide which was observed on hot-milling, and with the fact that the rate of breakdown of rubber is greater when the rolls are cool than when they are hot.

ADDITION OF PEROXIDES TO RUBBER ON THE MILL. If the breakdown of rubber on the mill is a chemical reaction involving activated oxygen, one might expect the reaction to go faster if a peroxide were added to the rubber on the mill. It was found that the addition of 5 cc. of hydrogen peroxide to 300-gram batches of smoked sheets increased the plasticity, as shown in Table I. All plasticity measurements reported in this paper are made at 100° C. with the Goodrich plastometer (*12*).

TABLE I. EFFECT OF ADDING PEROXIDE TO RUBBER ON THE MILL

MILLING TIME *Minutes*	MATERIAL ADDED *5 Cc.*	PLASTICITY AFTER MILLING
6	Water	11.4
6	Peroxide	13.9
10	Water	46.0
10	Peroxide	70.4

The addition of larger amounts of peroxide had a greater effect. As would be expected from the photographic tests, the addition of 5 cc. of hydrogen peroxide to a 300-gram batch of sprayed latex had less effect on the plasticity.

MASTICATION OF RUBBER IN PRESENCE OF VARIOUS GASES. As a final check on the theory, samples of rubber were milled in a Day internal mixer fitted with an air-tight cover, through which various gases could be passed. Rubber in 500-gram batches was milled 20 minutes, using Banbury-type blades in the mixer. Prime smoked sheets were milled in air, oxygen, and hydrogen. Hard sprayed latex was also tested, since it acted very differently from smoked sheets in the photographic peroxide tests. It was milled in air, oxygen, hydrogen, nitrogen, and carbon dioxide. No attempt was made to remove the air from the rubber, and the gases other than air were used directly from the cylinder without any purification. It was expected that there would be enough oxygen in the rubber and the gases to produce some softening, but it was anticipated that the amount of softening due to these traces of oxygen would be small.

Two or three batches of each rubber were masticated in oxygen and hydrogen, and single batches in the other gases. The different gases were used in random order, and, to prevent any gradual changes in temperature or other conditions from introducing systematic errors, the duplicate batches with the same gas were never run consecutively. Duplicate plasticity determinations were made on each batch. The average plasticity of all samples of each rubber was determined, as well as the average deviation of the single plasticity measurements. Table II shows the results obtained.

Table II. Plasticity of Rubber Milled in Various Gases

Gas	Smoked Sheets Batches	Smoked Sheets Plasticity	Sprayed Latex Batches	Sprayed Latex Plasticity
Unmilled	.	4.5 ± 0.2	.	1.5
Oxygen	2	18.9 ± 0.8	2	6.6 ± 0.6
Air	1	22.1 ± 0.4	1	9.0 ± 0.6
Hydrogen	2	5.9 ± 0.6	3	2.9 ± 0.5
Nitrogen	.	.....	1	1.8 ± 0.1
Carbon dioxide	.	.....	1	2.5 ± 0.1

The data show conclusively that the major part of the breakdown of smoked sheets in the internal mixer is not due to a mechanical breaking up of the molecules (as suggested by Staudinger) or to a mechanical breakdown of micelles or aggregates (as is commonly believed) but to an oxidation process; and the same conclusion should hold for smoked sheets broken down on the mill. Since the sensitivity of the plastometer is not very great at the lower end of the scale, the data for sprayed latex are more scattered, but they indicate that at least the major part of the breakdown which occurs when this rubber is milled is due to an oxidation process. The single batches milled in air had higher plasticities than those milled in oxygen, but the difference is not significant. It may have been due to slight temperature changes during the mastication or to a variation in the original rubbers. Later experiments indicate that milling in oxygen is as effective as milling in air.

To make a more drastic test of the theory, a few batches were milled in purified hydrogen and nitrogen for periods of 2 and 4 hours in the same mixer used for the above tests. To reduce the amount of oxygen dissolved in the rubber, the samples were kept in an atmosphere of nitrogen for from 2 to 4 days before the tests, and they were exposed to the air for as short a time as possible when they were transferred to the mixer. The nitrogen was purified by bubbling through alkaline pyrogallol, and the hydrogen was purified by passing over hot platinized asbestos. The results of these tests and of one experiment in which rubber was milled in oxygen are shown in Table III.

Table III. Effect of Milling for Long Times in Purified Gases

Kind of Rubber	Gas Used in Milling	Time of Milling	Plasticity Before milling	Plasticity After milling
		Hours		
Smoked sheets	Oxygen	2	3.3	64.6
Smoked sheets	Hydrogen	2	3.0	6.6
Smoked sheets	Hydrogen	4	3.1	6.1
Smoked sheets	Nitrogen	2	2.8	6.3
Sprayed latex	Nitrogen	2	2.1	3.1

Even these long times of milling did not greatly change the plasticity of the samples if oxygen was excluded, but milling the rubber in oxygen made it very plastic.

When acetone-extracted rubber was used, the effect of oxygen in milling was even more striking. A sample of extracted smoked sheet, having a plasticity of 7.0, was milled in oxygen for 20 minutes, after which its plasticity was 58.9; another sample milled in nitrogen for the same time had a plasticity of only 9.5.

Shacklock (*20*) recently measured the surface tension of solutions of rubber broken down in various ways, in an attempt to distinguish between a depolymerization and a disaggregation of the rubber. It would be very surprising if a straight depolymerization of the rubber would have much effect on the surface tension of a benzene solution, for most hydrocarbons with a density around 0.9 have a surface tension very close to that of benzene. Hence the small amount of depolymerization necessary to account for the change in physical properties would not be expected to change the surface tension of the solution. However, if rubber were broken down through an oxidation process, the oxidation product, whether a peroxide, acid, aldehyde, or alcohol, might be different enough chemically from the hydrocarbon to have an appreciable effect on the surface tension. Shacklock's results show that the cold-milling of rubber had more effect on the surface tension of the solutions than any other treatment, and hot-milling came next; but heating the rubber or exposing the solution to ultra-violet light had no effect. This is consistent with the view that the compounds formed in the rubber during milling are more polar (perhaps because there are more peroxides) than the compounds formed on heating the rubber or exposing the solution to light.

Since this paper was first submitted, the report of Cotton (*2*) on the mastication of rubber in the absence of oxygen was received. He found that milling in an atmosphere of nitrogen was much less effective than milling in oxygen, as was found in the work reported above. Both Cotton and Shacklock emphasize the effects of ozone and ionized oxygen in breaking down the rubber, and they imply that the mechanical action which occurs on milling is important chiefly because it causes the formation of ozone and ionized oxygen. They do not recognize so clearly the importance of the mechanical distortion in activating the rubber molecules, but in other respects their views are similar to those presented above.

SUMMARY

The effects of milling and of exposure to light are similar in altering smoked sheet, pale crepe, and balata so that they affect a photographic plate in the dark. This effect is due to the formation of a volatile peroxide, probably hydrogen peroxide. No image is formed by sprayed latex, fine Para, anode rubber, or guayule after being milled or exposed to the light.

The order of the intensity of the images formed by smoked sheets, pale crepe, and sprayed latex is the same as the order of their rate of change of plasticity on milling. Cold-milling is more effective than hot-milling, both in the formation of the peroxide and the breakdown of the rubber. Milling on a cold mill produces a luminous discharge from the blanket to the bank, but this disappears when the rolls are heated.

Sprayed latex and fine Para contain some material which decomposes hydrogen peroxide. This accounts for the fact that peroxides could not be detected in these rubbers, either after exposure to light or after milling, even with the addition of hydrogen peroxide. Both copper and cobalt soaps decompose the peroxide in some instances, though under other conditions the cobalt soaps greatly increase the amount of peroxide in the rubber.

A chemical reaction between rubber (activated through the mechanical deformation) and oxygen (activated by electrical charges) is advanced as a theory to account for the formation of peroxides and for most of the breakdown of rubber during milling.

The theory is supported by the peroxide tests, by the luminescence effects on milling, and by the fact that the mechanical working of rubber produces, at the most, only a small change in plasticity if the rubber is worked in the absence of oxygen.

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Stability of Chlorohydrocarbons

I. Methylene Chloride

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METHYLENE chloride, a low-boiling chlorohydrocarbon, has found extensive use as a refrigerant in air conditioning, and as a solvent for cellulose acetate, as a general low-boiling solvent, and as an intermediate in organic synthesis. It does not form explosive mixtures with air, and on this account may be useful where a safe low-boiling solvent is required. The present paper discusses the stability of methylene chloride alone or in contact with various substances and over a wide range of temperatures, and the possibility of corrosion of the common metals by methylene chloride.

The physical properties of methylene chloride are as follows:

Formula	CH_2Cl_2
Molecular weight	84.92
Color	Water-white
Odor	Sweet, pleasant, similar to chloroform
Sp. gr. (20°/4° C.)	1.3361
Freezing point, ° C.	−96.7
Boiling point (760 mm.), ° C.	39.8
Surface tension against air (18° C.), dynes/cm.	26.52
Refractive index	1.4234
Coefficient of viscosity (20.53° C.)	0.004414
Solubility in 100 grams H_2O (20° C.), grams	2.000
Specific heat	0.287
Latent heat of vaporization, cal./gram (B. t. u./lb.)	75.3 (135.8)
Critical temperature, ° C.	245.1

Experimental Procedure

Glass tubes, 2.5 by 25 cm., were prepared and provided with a 5-mm. constriction to facilitate sealing. Each of these tubes received 25 cc. of methylene chloride, distilled in an atmosphere of nitrogen prior to the experiment; and, where specified, water, oxygen, and metal strips were also added (as shown in Tables I and III). A series of these glass tubes was placed inside capped iron pipes; and these were then immersed in electrically heated oil baths, maintained at 40°, 60°, 80°, 100°, 120°, and 140° C., ± 2°, for 24 hours.

After cooling, the tubes were opened and the contents transferred to a titration flask, 25 cc. of neutral distilled water added, and any developed acidity titrated with 0.01 *N* alkali, using phenolphthalein as indicator. The results are given in Table I.

The metal strips were cleaned, polished, rinsed with methylene chloride, and weighed. After removal from the glass tubes, the strips were wiped clean and weighed. The loss in weight per square centimeter of surface is tabulated in Table II.

The methylene chloride used throughout this investigation was a commercial grade conforming to the following specifications:

Acidity	None
Boiling range (760 mm.), ° C.	39.5–39.8
Residue on evaporation	Faint trace
Moisture	None
Color	Water-white
Odor	Normal

Discussion of Results

In this study it was assumed that the decomposition of methylene chloride is proportional to the amount of free acid formed. This is not strictly true, since decomposition may occur without forming free acids; furthermore, if free acids are formed, they may combine with polymerized decomposition products to give neutral substances. For the purpose of the present investigation, however, the acidity developed gives data of real value.

Effect of Temperature on Decomposition of Methylene Chloride. No decomposition occurred below 120° C. when methylene chloride was heated for 24 hours in sealed tubes. At 120° C., 1.2 cc. of 0.01 *N* hydrochloric acid for 25 cc. was found, indicating that methylene chloride is stable at these temperatures. At 200° C. an acidity of 0.0002 per cent by weight of hydrochloric acid developed when the vapor of methylene chloride was passed through an iron tube with a contact time of 1 to 3 seconds. This decomposition is negligible. At 300° and 400° C. the acidity amounted to only 0.0032 and 0.0115 per cent by weight. At 500° C., marked decomposition occurred. The acidity at this temperature amounted to 0.044 per cent by weight of hydrochloric acid.

Effect of Water on Decomposition of Methylene Chloride. Hydrolysis of methylene chloride would be expected to result in the formation of hydrochloric acid and formaldehyde; therefore, wherever moisture was present in a determination, Schiff's test for formaldehyde was applied.

The amount of water present has a decided influence on the decomposition of methylene chloride. With just enough water to saturate it at room temperature, decomposition was observed at 100° C. At 120° and 140° C. this decomposition was slightly greater. No formaldehyde was found when using Schiff's reagent. With an excess of water (1 mole of methylene chloride to 2 moles of water) hydrolysis started at 60° C., about 20° above the boiling point of the solvent;

this increased rapidly with temperature, so that at 140° C. 2281 cc. of 0.01 *N* hydrochloric acid had formed, indicating that about 3.4 per cent of the methylene chloride was hydrolyzed in 24 hours. Positive test for formaldehyde indicated its presence. No hydrolysis occurred at the boiling temperature. Methylene chloride was refluxed for 8 days in the presence of 1.5 per cent water, with no development of acidity.

EFFECT OF OXYGEN ON DECOMPOSITION OF METHYLENE CHLORIDE. Pure oxygen or oxygen in the air had no apparent effect on methylene chloride below 140° C. This is striking when it is recalled that chloroform is readily decomposed by atmospheric oxygen.

EFFECT OF METALS ON DECOMPOSITION OF METHYLENE CHLORIDE. Dry methylene chloride, or methylene chloride saturated with water, was not decomposed by soft steel on heating to 120° C. in sealed tubes for 24 hours. Methylene chloride was not decomposed on refluxing with steel in the presence of about 1.5 per cent water for 8 days. No decomposition was observed when methylene chloride was heated for 24 hours in an atmosphere of oxygen or air up to 120° C. in the presence of soft steel.

TABLE I. DECOMPOSITION OF METHYLENE CHLORIDE UNDER VARIOUS CONDITIONS

(In cc. of 0.01 *N* HCl per 25 cc. CH_2Cl_2[a])

EXPERIMENTAL CONDITIONS	DECOMPOSITION ON HEATING 24 HOURS AT:					
	40° C.	60° C.	80° C.	100° C.	120° C.	140° C.
Methylene chloride in nitrogen:						
Dry	0	0	0	0	1.20	...
With soft steel	0	0	0	0	0	...
Satd. with water	1.30	0	0	6.55	4.65 28.75	...
With soft steel, satd. with water	..	0	0	0	0.40	0.35
With copper, satd. with water	..	0	0	0	0	0
With aluminum, satd. with water	..	0	1.40	0.40	..	0.45
With lead, satd. with water	..	0	0.6	0.70	0.45	0
With tin, satd. with water	..	0	0.4	0	0	2.45
With brass, satd. with water	..	0	0	0	1.45	291.0
With excess of water	..	1.55	3.55	45.40	287.0	2281.0
With soft steel and excess of water	..	3.55	41.15	196.0	272.0	...
Methylene chloride and soft steel in air	..	..	0.15	0.20	0.45	22.00
Methylene chloride with 1.5% water, refluxed with soft steel for 24 hours	(Acidity—none)					
Methylene chloride with 1.5% water, refluxed with soft steel for 8 days:	(Acidity—0.05 cc.)					
Soft steel in oxygen	..	0.15	0.10	0.75	0	0.25
Soft steel, satd. with water in oxygen	..	0	0.10	80.7	80.90	...

[a] 1 cc. of 0.1 *N* HCl per 25 cc. of solvent is equivalent approximately to 0.001% by weight of HCl.

TABLE II. VAPOR-PHASE DECOMPOSITION OF METHYLENE CHLORIDE

Temperature, ° C.	200	300	400	500
0.01 *N* alkali, cc.	0.05	2.99	10.56	40.11
HCl by weight, %	0.0002	0.0032	0.0115	0.044

Copper, aluminum, brass, tin, and lead had no effect on the decomposition up to 140° C. Methylene chloride was not affected by these metals to any marked extent.

COMBINED INFLUENCE OF WATER AND METALS ON DECOMPOSITION OF METHYLENE CHLORIDE. The influence of each of these factors has already been noted. The combined influence of both water and metals on the decomposition of methylene chloride is negligible up to 120° C. if just enough water is present to saturate the methylene chloride. In the presence of an excess of water and soft steel, the decomposition of methylene chloride is more extensive than if water alone is present in excess. For instance, at 80° C. the acidity was 3.5 cc. of 0.01 *N* hydrochloric acid per 25 cc. when water alone was present in excess. With excess water and soft steel, the acidity was 41.2 cc. of 0.01 *N* hydrochloric acid at the same temperature. No decomposition was observed when the solvent was refluxed with 1.5 per cent of water and soft steel for 8 days. Decomposition occurred only at temperatures above the boiling point of this solvent.

TABLE III. CORROSIVE EFFECT OF METHYLENE CHLORIDE ON VARIOUS METALS

(In milligrams per square centimeter)

EXPERIMENTAL CONDITIONS	CHANGE IN WEIGHT ON HEATING 24 HOURS AT:				
	60° C.	80° C.	100° C.	120° C.	140° C.
Methylene chloride and:					
Soft steel, in nitrogen	−0.03	0	0	0	...
Soft steel satd. with water, in nitrogen	0	0	0	+0.05	+0.05
Soft steel, excess water, in nitrogen	−0.1	−0.67	−3.1	−1.4	[a]
Soft steel, in air	0	0	0	0	0.013
Soft steel, in oxygen	0	0	0	0	0
Soft steel satd. with water, in oxygen	−0.1	−0.4	−1.57	−3.0	[a]
Soft steel, 1.5% water, refluxed 48 hours	(Very slight)				
Soft steel, 1.5% water, refluxed 8 days	(Very slight)				
Copper satd. with water, in nitrogen	0	0	0	0	0
Aluminum satd. with water, in nitrogen	0	0	0	0	0
Lead satd. with water, in nitrogen	0	−0.2	0	−0.1	0
Brass satd. with water, in nitrogen	0	0.10[b]	0[b]	0[b]	1.5[b]
Tin satd. with water, in nitrogen	0	0	0	0	2

[a] Heavy coat of iron oxide. [b] Copper-colored surface.

CORROSIVE EFFECT OF METHYLENE CHLORIDE. Aluminum, copper, tin, lead, and soft steel were not corroded by dry methylene chloride or methylene chloride saturated with water up to 140° C. The loss in weight of these metals was well within the experimental error for each determination. Brass was attacked at 60° C., changing the surface to bright copper-like color, indicating that the zinc was dissolved. Soft steel was not corroded with methylene chloride on refluxing with an excess of water for 8 days. At higher temperatures the solvent with an excess of water corroded soft steel owing to hydrolysis. Methylene chloride is the least corrosive of the higher chlorinated hydrocarbons. Its corrosive effect is hardly greater than that of water.

SUMMARY

1. Methylene chloride has been found to be stable up to 120° C., about 80° above its boiling point.
2. Small quantities of water do not appreciably affect the stability of methylene chloride at temperatures below 100° C.
3. The presence of an excess of water causes no decomposition of methylene chloride at its boiling point; at higher temperatures, some decompositions take place.
4. Soft steel, copper, aluminum, lead, and tin have no effects on the decomposition of methylene chloride. Brass, up to 80° C., has a negligible effect.
5. The combined influence of water and soft steel, copper, aluminum, lead, brass, and tin does not affect decomposition of methylene chloride at temperatures up to 100° C.
6. Pure oxygen or oxygen from the air has only a slight effect on the decomposition of methylene chloride up to 120° C.
7. The combined effect of oxygen and soft steel on the decomposition of methylene chloride is negligible even at 140° C.
8. The combined effect of soft steel, oxygen, and moisture on the decomposition of methylene chloride is negligible up to 80° C.
9. Various metals, such as soft steel, aluminum, copper, tin, and lead, are not corroded by methylene chloride saturated with water. Brass is attacked above 60° C.

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Temperature Coefficient of Vulcanization

Determination for Mixes Accelerated with Mercaptobenzothiazole and a Crotonaldehyde-Aniline Condensation Product

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THE TEMPERATURE of the inside of a rubber article during vulcanization is much lower than that of the outside because of the low heat conductivity of rubber compounds. Since the curing intensity depends upon the temperature, the cure of the inside of the article is often widely different from that of the outside. In order to evaluate the cure, it is necessary to know accurately how curing intensity varies with temperature. Satisfactory data for mercaptobenzothiazole stocks have been lacking.

The temperature coefficients have been determined for mercaptobenzothiazole mixes and for a mix accelerated by a crotonaldehyde-aniline condensation product. Special care was taken to eliminate errors in temperature regulation, etc., by the use of thermocouples in the samples during cure. The values derived from modulus and combined-sulfur data were found to be 1.91 and 2.30 (av.), respectively, for mercaptobenzothiazole; and 2.32 and 2.67, respectively, for crotonaldehyde-aniline.

DATA accumulated over a considerable period have indicated that, when employing certain accelerators, the temperature coefficient of vulcanization is not the same as when a rubber-sulfur mix is used. The values obtained in the past have been subjected to considerable criticism, and curing results from tires have indicated that the values commonly used for stocks containing mercaptobenzothiazole were too high. The values used have varied for different experimenters between 1.45 and 1.60 per 10° F., or 1.94 to 2.35 per 10° C. In some quarters it seems to have been the practice to use the same temperature coefficient regardless of the type of mix or type of accelerator employed. The present experimental work was conducted with the purpose of determining more accurately the value of the temperature coefficient for mercaptobenzothiazole mixes.

In the procedure of vulcanizing test samples, there are several conditions which introduce errors of some magnitude. Two of these errors were thought to be important enough to warrant the correction of the data:

1. It has frequently been observed that the test sheets do not attain the temperature registered by the press thermometer.
2. When a mold is removed from the vulcanizing press for refilling, it drops considerably in temperature. When it is replaced in the press, some minutes elapse before the mold regains the equilibrium temperature. This mold lag may reduce the effective curing time.

The first of these errors may be reduced to a large extent by proper adjustment of the press temperatures. The second is a difficulty inherent in the curing method. Both may be corrected by following the temperature of the test sample with a thermocouple.

No previous data were available regarding the effect of varying sulfur or accelerator ratios, or the effect of the quantity of pigment used in the mix.

Experimental Procedure

With a view to supplying information on the above points, eight stocks were prepared according to the formulas shown in Table I. It may be seen that these stocks include a number of the common variations to be expected in tire stocks. A large enough batch of each stock was mixed to fill all the curing requirements. Sheets were then cut and stored for use. A two-opening hydraulic press was selected after exploration of the platens with a "thermoboard." This device makes it possible to determine the temperature of a small area of the platen and compare it with the temperature of similar areas over the platen surface. Thermocouples at the surface of the thermoboard were used directly in contact with the platen surface. The check was repeated at each temperature used. The press selected had the smallest temperature variation of any press available (maximum, 1° F. or 0.55° C.).

A range of cures was made at each of a series of temperatures separated from each other by steps at 10° F. (5.56° C.). The sheets were cured in four-cavity steel molds, meeting the recommendations of the Physical Testing Committee of the Rubber Division, American Chemical Society. One mold was placed in each opening of the press, allowing eight sheets to be cured at one time. Before loading the mold, a thermocouple was inserted in each sheet. Each couple was placed in such a way as to be as nearly as possible at equal distances from the flat surfaces of the mold and in the center of the sheet. The time required to load the molds was considerably increased by this procedure, approximately 10 minutes being consumed in inserting the sheets in the mold and placing the mold in the press. This practice was followed in all cures up to and including the 250° F. (121° C.) series. The duplication of temperatures from sheet to sheet was so good that from 260° F. (125° C.) to 310° F. (154.4° C.) only one couple was used in a single sheet placed always in the same stock and in the same mold cavity. This reduced the time of loading of the molds to about 3 minutes and hence reduced the temperature lag due to mold radiation.

Table I. Compositions of Stocks

	Stocks							
	A	B	C	D	E	F	G	H
Pale crepe	100	100	...	100	100	100	100	100
Extracted pale crepe	...	...	100	...	...	...	...	...
Mercaptobenzothiazole	0.3	0.3	0.3	0.2	0.7	0.7	1.0	...
ZnO	5	5	5	5	131	131	5.0	5
Sulfur	3	3	3	6.0	3	3	3	3
Stearic acid	...	4.0	1.5	...	...	4.0	4.0	...
Carbon black	...	...	...	...	...	...	40	...
Crotonaldehyde-aniline condensation	...	...	...	...	...	...	...	1

The effect of the temperature lag of the molds was much smaller than was anticipated. The time required for the sheet to reach temperature equilibrium was 5 to 7 minutes. In order to convert these values to equivalent cure units at the scheduled temperature, a time-intensity curve was drawn for each cure, using a preliminary value of 1.50 for the temperature coefficient of vulcanization. From this curve, with the aid of a planimeter, the equivalent cure was computed. The method used has been outlined in detail

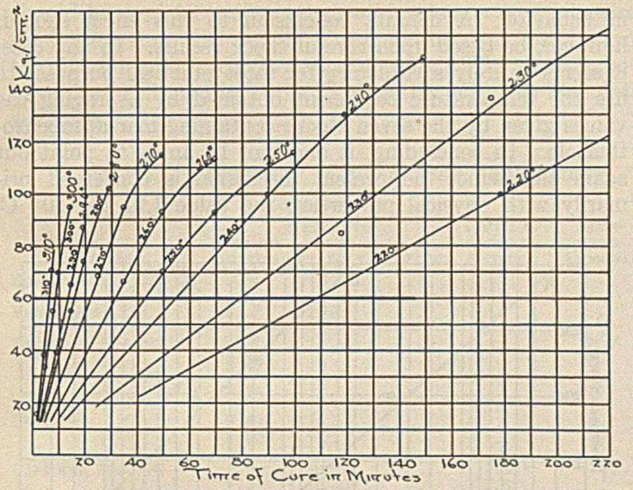

Figure 1. Stock C

by Sheppard and Wiegand (*4*). In spite of the time required to reach temperature equilibrium, the reduction in equivalent cure in no case amounted to more than 3 minutes at the temperature used. In most cases it was less than 1 minute. This amounts to about 1 to 2 per cent of the total equivalent cure at temperatures up to 250° F. (121° C.). At higher temperatures the percentage loss in equivalent cure was higher because of the shorter times of cure. Differences in equivalent cure in a given time between two individual cures at the same temperature never amounted to more than 2 per cent. In practically all cases, at a given temperature the curves relating intensity of curing effect with time were identical during the period of rise. Mold lag, although taken into consideration in the plotting and calculation of data, affected the results to a very small extent. For example, stock C calculated from the curve as drawn in Figure 4 gives a value of 1.764; stock C calculated from the curve uncorrected for mold lag gives a value of 1.750. The equilibrium temperatures reached by the sheets in the press were in all cases so close to the temperatures scheduled as to produce no measurable effect on the results.

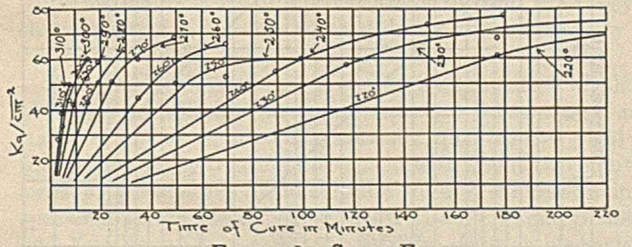

Figure 2. Stock F

After curing, the sheets were tested, using the Goodyear testing machine. Combined sulfur data were obtained on a sufficient number of sheets to determine the temperature coefficient. The combined sulfur data are given in Table II.

Table II. Combined Sulfur

Stock	2.3/ 310°	4.6/ 300°	9.1/ 290°	14.25/ 280°	24.25/ 270°	34.25/ 260°	69.7/ 250°	89/ 240°	117.5/ 230°	178.2/ 220°
	Cure in Minutes at Temperature Specified (° C.)[a]									
	%	%	%	%	%	%	%	%	%	%
A	0.38	0.82	0.75	0.74	0.58	0.77	0.55	0.82	0.68	0.72
B	0.24	0.51	0.45	0.52	0.38	0.49	0.55	0.53	0.45	0.48
C	0.45	0.75	0.58	0.71	0.53	0.80	0.83	0.81	0.61	0.70
D	0.52	0.80	0.65	0.74	0.64	0.85	0.85	0.88	0.67	0.38
E	0.41	0.59	0.48	0.74	0.42	0.64	0.62	0.67	0.54	0.58
F	0.28	0.37	0.34	0.96	0.34	0.42	0.36	0.44	0.34	0.68
G	0.41	0.56	0.54	0.52	0.48	0.62	0.81	0.55	0.44	0.34
H	0.82	0.83	0.92	0.89	0.88	0.78	0.74	0.69	0.54	0.50

[a] The cure as given has been corrected for temperature lag of the mold.

Combined sulfur was determined as follows:

> A 0.5-gram sample of the stock was extracted overnight in an Underwriter's apparatus. The extracted stock was then transferred to an Underwriter's flask. A mixture of concentrated nitric acid saturated with bromine was added, and digestion carried out at low heat until the bromine fumes were completely expelled. The volume was reduced to 20 cc., and 3 grams of potassium chlorate were added. The solution was then evaporated to dryness. Expulsion of nitric oxide was accomplished by repeatedly evaporating to dryness after addition of hydrochloric acid. The sulfates were then precipitated and ignited in the usual way.

Calculation and Discussion

Modulus may be determined with a greater degree of accuracy then tensile, elongation, or any other commonly used characteristic of the stress-strain curve. For this reason modulus alone was used in calculating the temperature coefficient. In any given case the elongation at which modulus studies were to be made was chosen arbitrarily for convenience in plotting. The elongation selected for study of stock C was 800 per cent. Values used for other stocks are shown in the line labeled "Strain" in Table III. The modulus values, read from the stress-strain curves at the chosen elongation, were plotted as modulus-time curves of the type shown in Figures 1 and 2. Figure 1 shows stock C and Figure 2 shows stock F. Similar curves were drawn for each stock. At each temperature the time of cure required to produce a given modulus was read from these curves.

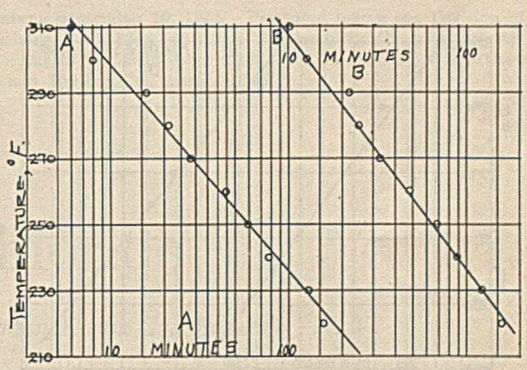

Figure 3. Time of Cure for Standard Physical Properties

Stocks A and B

In the case of stock C, for example, the times read were those required to produce a modulus of 60 kg. per sq. cm. The times of cure so determined were plotted in Figures 3 to 6, against the temperature. The above method is the one in most common use and has been outlined in a previous paper (*1*). A similar procedure was used with the combined sulfur data (Figures 7 to 10).

The temperature coefficients have been calculated (*3*) from these curves and are given in Table III.

Table III. Temperature Coefficients

	A	B	C	D	E	F	G	H
	Stocks							
	Calculated from modulus data							
Strain, %	800	800	800	800	400	400	300	700
Coefficient (10° F.)	1.45	1.38	1.37	1.41	1.45	1.46	1.52	1.60
Coefficient (10° C.)	1.94	1.79	1.76	1.86	1.96	1.97	2.13	2.32
	Calculated from combined sulfur							
Coefficient (10° F.)	1.60	1.56	1.55	1.60	1.55	1.57	1.65	1.72
Coefficient (10° C.)	2.34	2.28	2.21	2.34	2.21	2.25	2.46	2.67

It is an outstanding fact that the temperature coefficient calculated from physical data is lower than that calculated from combined sulfur data. It is obvious from an inspection of Table II and the individual temperature-coefficient plots, that the combined sulfur data were not as reliable as the physical data. Nevertheless, the differences between the coefficients as calculated from the two sets of data are consistent enough both in direction and magnitude to indicate a definite difference. This being the case, it is evident that a value for the coefficient determined by means of combined sulfur data alone could not be satisfactorily used to predict physical cure. This is in agreement with the fact pointed out by Shepard and Krall (*2*) that degree of physical cure is not related to combined sulfur.

It has been noted frequently that various accelerators seem to have optimum curing temperatures. Figures 1 and 2 indicate that higher modulus values are developed at 220° F. (104.4° C.) to 240° F. (115.5° C.) than at higher temperatures. This behavior seems to be characteristic of stocks accelerated with mercaptobenzothiazole. The data for stock H indicated a much higher optimum. No similar optimum was found for a rubber-sulfur mix (*1*), nor was there any difference between the temperature coefficient derived from physical data and the coefficient calculated from combined sulfur.

The variations in the individual values obtained from the various stocks from A to G may represent an actual difference in behavior. A definite conclusion to this effect should, however, be based upon careful check results. In any case, it seems entirely satisfactory for most practical purposes to use the temperature coefficient obtained by averaging the values given by the seven stocks containing mercaptobenzothiazole. In concluding, it may not be amiss to point out again that, since the present discussion is concerned primarily with physical properties; the value 1.91 per 10° C.

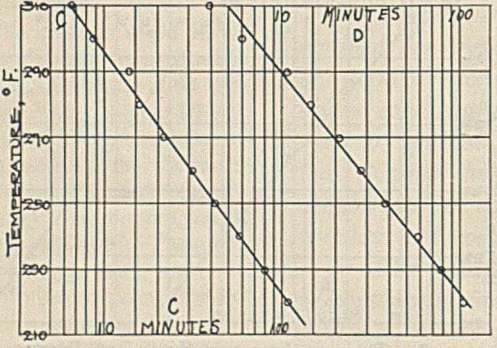

Figure 4. Stocks C and D

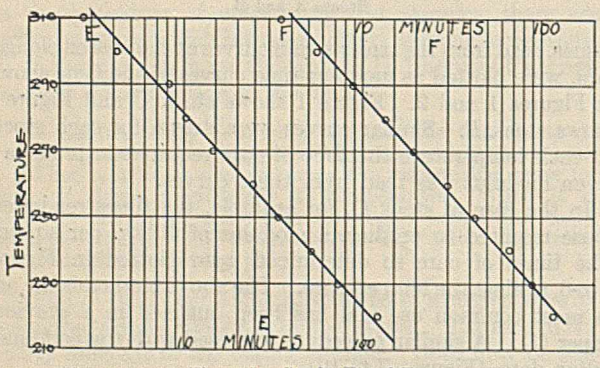

Figure 5. Stocks E and F

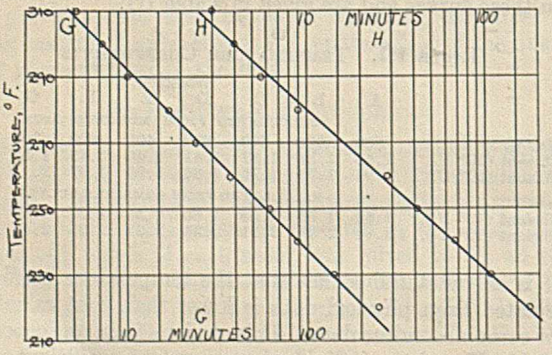

Figure 6. Stocks G and H

Time of Cure for Standard Modulus

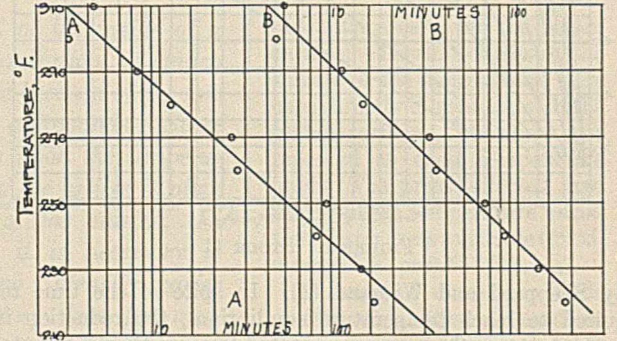

Figure 7. Stocks A and B

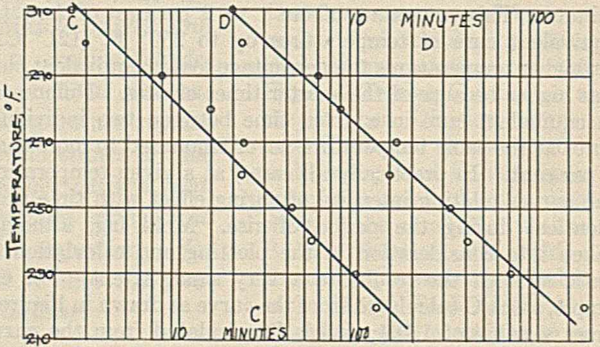

Figure 8. Stocks C and D

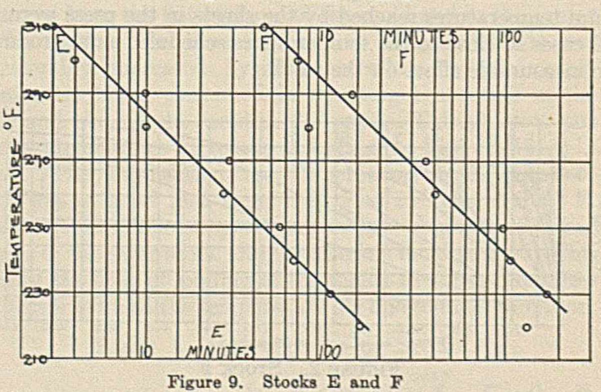

Figure 9. Stocks E and F

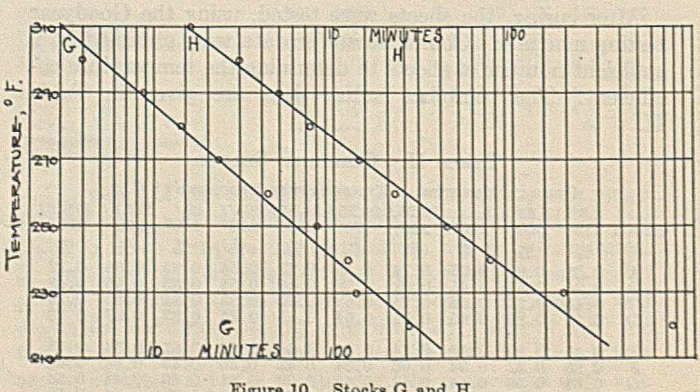

Figure 10. Stocks G and H

Time of Cure for Standard Combined Sulfur should be used for mercaptobenzothiazole stocks. Likewise, the lower value, 2.32 per 10° C., should be used for the crotonaldehyde-aniline condensation product. The above values have been collected in Table IV, together with the best data available in the literature.

TABLE IV. VALUES OF TEMPERATURE COEFFICIENT
(At 10° C.)

AUTHORITY	RUBBER SULFUR	MERCAPTO-BENZO-THIAZOLE	LITHARGE	CROTON-ALDEHYDE-ANILINE	ALDE-HYDE-AMMONIA
Spence and Young (*5*)	2.65^a	..	..	..	..
Van Rossem (*7*)	$2^{\ a}$	..	..	..	..
Twiss and Brazier (*6*)	2.3^a	..	..	..	2.4^c
	2.3^b	..	..	..	..
	2.4^b	..	..	..	..
	2.6^c	..	..	..	..
Park (*1*)	2.50^b	..	..	..	..
	2.50^a	..	..	..	..
Park and Maxwell	..	1.91^b	..	2.32^b	..
	..	2.30^a	..	2.67^a	..
Sheppard (*3*)	..	..	2.59^c	..	..

[a] Combined sulfur. [b] Physical data. [c] Average value.

CONCLUSIONS

1. The average temperature coefficient of mercaptobenzothiazole accelerated mixes, based upon physical data, was found to be 1.91 per 10° C. For crotonaldehyde-aniline, the value was 2.32 per 10° C.

2. Based upon combined sulfur data, the value was 2.30 (average) per 10° C., and for crotonaldehyde-aniline 2.67 per 10° C.

3. The values obtained from physical data are to be preferred for all practical purposes.

ACKNOWLEDGMENT

The authors are indebted to H. W. Wilson for assistance in the experimental work, and to R. P. Dinsmore for kind permission to publish the results.

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Furoyl Chloride

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IN RECENT years furfural (2-furaldehyde) has become inexpensive and easily available in large quantities. The drop in price of furfural has stimulated research in the field and has produced correspondingly inexpensive derivatives, such as furoic (pyromucic) acid. Furoyl chloride[1] is one of the most useful derivatives of furfural from a synthetic viewpoint because of its stability and multiplicity of reactions.

Furoyl chloride was first prepared by the action of phosphorus pentachloride on furoic acid (*6*). Frankland and Aston (*3*) have reported a practically quantitative yield of furoyl chloride by treating furoic acid with about two equivalents of phosphorus pentachloride in dry chloroform in a special apparatus described by them. Baum (*1*) and Gelissen and Van Roon (*4*) have prepared furoyl chloride by heating the acid with thionyl choride on a water bath over a period of 1 to 2 hours. The yields were reported to be nearly quantitative. Bogert and Stull (*2*) using the same method, reported a yield of 79 per cent. Maxim (*7*) obtained a 40 per cent yield of furoyl chloride by treating the acid with thionyl chloride, and a yield of 70–80 per cent by the action of phosphorus pentachloride on the acid. Gilman and Hewlett (*5*) prepared the acid chloride in 75 per cent yield by treating the acid with thionyl chloride in dry benzene.

An examination of the literature indicates that the yield of the acid chloride obtained by treating the acid with phosphorus pentachloride or thionyl chloride is variable. There is the possibility that decomposition is caused by impurities in the acid itself or in the reagents used.

EXPERIMENTAL

The preparation described here is an extension and modification of the method of Gilman and Hewlett (*5*). It is believed that the method described is applicable to quantities many times that described in this report.

The reaction was carried out in a 22-liter flask fitted with an inverted Liebig condenser, an S-tube, and a dropping funnel for the introduction of the thionyl chloride, and suitable means for removing the hydrogen chloride and sulfur dioxide which were evolved in the preparation. Five thousand six hundred grams (50 moles) of a commercial grade of furoic acid[2] were placed in the flask, and 10 liters of dry benzene[3] added. The reaction mixture was then placed on a steam bath and heated to gentle refluxing, and 8294 grams (75 moles) of a commercial grade of thionyl chloride were added dropwise over a period of 4 days. The reaction mixture was not heated overnight. After the addition of the thionyl chloride, the reaction mixture was refluxed for an additional 12 hours and filtered into a 22-liter flask. The flask was fitted with a 1.5-foot (45.7-cm.) fractionating column, and the benzene and excess thionyl chloride were distilled over on a steam bath. After removal of the benzene and thionyl chloride, the acid chloride was distilled from a 12-liter flask fitted with a 2.5-foot (76.2 cm.) fractionating column, Liebig condenser, and water-cooled 5-liter receiver. The first fraction boiling up to 59.5° C./7 mm. weighed 90–100 grams and was mostly

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[1] Attention is called to the fact that furoyl chloride is a vigorous lachrymator and must be handled with care.

[2] The crude acid was an air-dried material which contained 97 per cent furoic acid and about 2 per cent moisture.

[3] The benzene was dried by distilling a commercial grade of benzene through a 1.5-foot column until the distillate was no longer milky. About 15 per cent of the benzene was distilled over.

furoyl chloride. The yield was 5645 grams or 89.5 per cent[4] of the calculated amount of furoyl chloride boiling at 59.5–61.5° C./7 mm. The combined fore- and after-runs weighed 130–150 grams, in addition to a residue of about 100 grams of carbonaceous material.

The low- and high-boiling fractions were found to contain much furoyl chloride which could be recovered by redistillation. It was convenient to transform it to furamide by adding it to concentrated ammonia water.

Thus, furoyl chloride can be prepared on a semi-commercial scale in 89.5 per cent yield by the action of thionyl chloride on furoic acid in benzene.

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[4] The yield is based on the amount of furoic acid available.

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Heat Transfer in Stream-Line Flow

II. Experiments with Glycerol

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NEW DATA are reported for heat transfer to glycerol as it flows in stream-line motion through a horizontal, standard $^1/_8$-inch iron-pipe-size copper tube, steam-heated over 61.75 inches (156.8 cm.) of its length. The apparatus used, which is capable of unusual precision and has negligible heat losses, is described in detail.

On a plot of (temperature rise ÷ initial temperature difference) vs. Wc/kL, the runs with an initial temperature difference of 65° C. fall on a curve substantially higher than do runs with an initial temperature difference of 30° C. Both curves are higher than the theoretical line for zero temperature difference. For an initial temperature difference of 65° C. the curve for glycerol lies below that for a hydrocarbon oil.

IN THE first paper of this series (*4*, *5*) the present author, in collaboration with Hogan and McAdams, discussed the then available data on heat transfer from pipe to fluid for the case of modified stream-line flow of liquids in horizontal round pipes. Most of the experimental work examined had been carried out in steam-heated double-pipe apparatus so that the temperature of the tube wall was, in each case, substantially uniform. Hence, the results were properly comparable with the theoretical formula of Graetz (*7*) and Nusselt (*13*) which presupposes a constant temperature wall. It was shown that, although the theoretical equation failed considerably of representing the experimental results, the data of known reliability could be correlated with some degree of satisfaction by the use of the dimensionless coördinates suggested by the theory—$(t_2 - t_1)/T - t_1)$ and Wc/kL. In the range of modified stream-line motion, for a given Wc/kL and wall temperature, the observed temperature rise was larger than that predicted by the Graetz theory, which assumes a parabolic distribution of mass velocity. It was suggested that this effect was due to free convection currents.

The data at hand when the paper was written were, with the exception of a few tests on water, obtained by experimentation with hydrocarbon oils. In the two best and most complete investigations the same oil had been used. Therefore, the authors could in no way detect with certainty possible deviations between the results for various fluids. During the discussion (*4*) Sherwood reported a series of experiments by Kiley and Mangsen (*12*) on heating oil, and some work by Petrie (*14*) on heating *n*-butanol. The first of these sets of data agreed well with the empirical curve by which the authors had represented the results of Holden (*9*) and of White (*16*), both of whom worked with a similar oil. Since Kiley and Mangsen had used several different lengths of pipe, the agreement showed that variations in pipe length were properly accounted for by the proposed method of plotting if similar fluids alone were considered. The *n*-butanol data, although clearly of less reliability than those for oil, seemed to indicate a curve distinctly different from that defined by the oil data. As possible reasons for the discrepancy between *n*-butanol and the hydrocarbon oil, differences in Grashof number or in temperature-variation of viscosity were suggested.

The need for heat-transmission studies in the region of stream-line flow with fluids other than hydrocarbon oils, and in the turbulent range with fluids other than hydrocarbon oils, water, and air, has long been apparent. Partly to satisfy this need and partly to supply additional data on non-isothermal fluid friction in pipes, work was started in 1930 by Harrison (*8*), under the direction of C. S. Keevil,[1] to develop an apparatus that should satisfy the three following requirements:

1. It must be possible to make the necessary heat measurements with substantially calorimetric precision and reproducibility.
2. Perfect operation must be possible with no more than 1 gallon of fluid in the system so that the cost of the fluid may not limit one's choice.
3. Precise pressure-drop measurements must be possible over part of the heated length.

During 1930–31, Botzow and Wilson (*2*), continuing the work under the direction of the author, completely rebuilt Harrison's apparatus and succeeded in satisfying the first two requirements to a reasonable degree. These men were followed in the summer of 1931 by Rynalski and Huntington (*15*) who, after making several noteworthy improvements in the equipment, carried out a successful series of runs using glycerol as the fluid. Since these glycerol data show a distinct deviation from the line given previously for oils, and are of an unusually high order of reproducibility, it has seemed desirable to publish them immediately and to describe the apparatus with which they were obtained.

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[1] At present professor of chemical engineering, Oregon State Agricultural College, Corvallis, Ore.

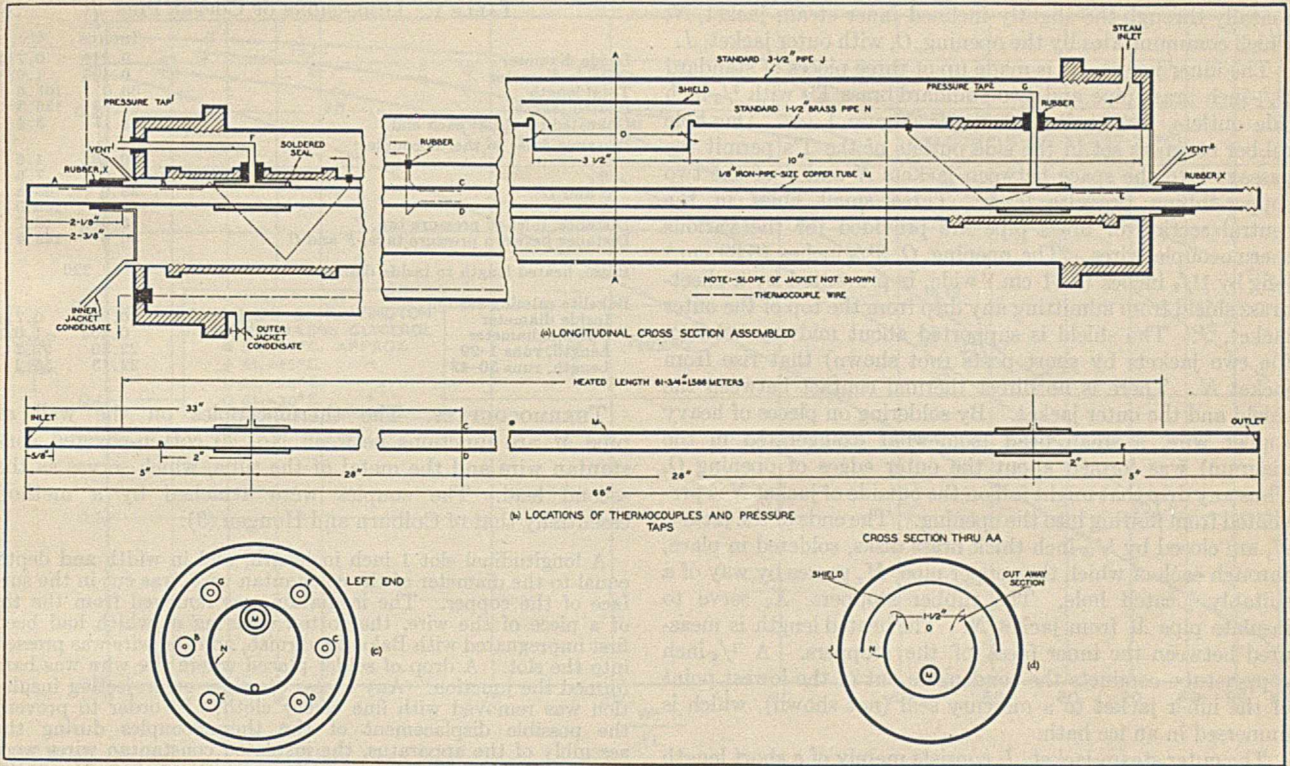

Figure 1. Diagram of Double-Jacketed Heat-Exchanger

Built by Botzow and Wilson (*2*) and used by Rynalski and Huntington (*15*), approximately to scale

Apparatus

The fundamental idea upon which the design of the apparatus is based was developed during the study of another problem in this laboratory—that of the peripheral variation of the heat flux from the outer surface of an internally heated pipe (*6*). A central pipe containing the cold fluid is surrounded by a steam jacket which is placed within a larger steam jacket. Condensate formed on the outer wall of the central pipe can be collected separately from the condensate in the larger steam jacket. In this way, if dry steam is supplied to the smaller jacket, the heat transferred by it to the outer walls of the inside pipe and thence to the fluid can be determined with precision, since the usual large correction for heat losses to the room is made negligible. The necessity for thus measuring the quantity of heat transmitted to the fluid arises from the difficulty of ensuring perfect mixing of the liquid before the thermometer at the outlet of the heat exchanger is reached. In stream-line flow experiments little reliance can be placed upon the rise in fluid temperature as measured directly, unless heat-balance data of accuracy are available to serve as a check.

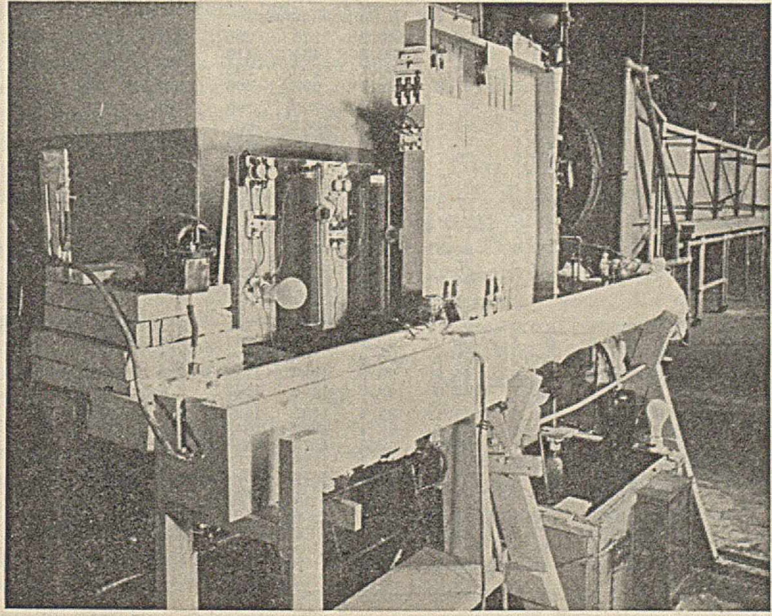

Figure 2. Assembled Apparatus Used by Rynalski and Huntington

Test Section. Figure 1 shows the heat exchanger in its present state. With the exception of air vent 2, which has been added since the completion of their work, the apparatus is as it was used by Rynalski and Huntington.

The fluid to be heated passes through the standard $^1/_8$-inch iron-pipe-size drawn copper tube, *M*, the dimensions of which are given in Table I and shown in Figure 1 (*b*). At 5 inches (12.7 cm.) and at 61 inches (154.9 cm.) from the inlet, four small holes, 90° apart, are drilled through the tube wall to serve as pressure taps. About each set of holes is a piezometer ring which was constructed by reaming out a $^1/_8$-inch brass T until it would slip over the copper pipe, and then soldering it in place over the holes with the side outlet projecting upward. Five thermocouples, *A*, *B*, *C*, *D*, and *E*, are affixed to the outer surface of the pipe at the locations shown. All except *D* are on the upper side of the pipe. *D* is diametrically opposite *C*. The copper pipe extends horizontally through the slightly inclined inner steam jacket, *N*, which communicates by the opening, *O*, with outer jacket, *J*.

The inner jacket, *N*, is made up of three pieces of standard $1^1/_2$-inch brass pipe and two standard brass T's with $^3/_8$-inch side outlets, arranged as shown in Figure 1 (*a*). One-hole rubber stoppers set in the side outlets of the T's permit the passage into the space between jackets *N* and *J* of the two copper-tubing pressure leads. Three small holes in the central section of brass pipe are provided for the various thermocouple wires. The opening, *O*, $3^1/_2$ inches (8.89 cm.) long by $1^1/_2$ inches (3.81 cm.) wide, is prevented by a sheet-brass shield from admitting any drip from the top of the outer jacket, *J*. The shield is supported about midway between the two jackets by short posts (not shown) that rise from jacket *N*. There is no direct thermal contact between the shield and the outer jacket. By soldering on pieces of heavy copper wire, a small bead (somewhat exaggerated in the diagram) was formed about the outer edges of opening *O*. Thus any drip that might fall on the outside of jacket *N* is prevented from flowing into the opening. The ends of the jacket, *N*, are closed by $^1/_{16}$-inch thick brass disks, soldered in place, through each of which the copper pipe, *M*, passes by way of a suitably located hole. The rubber stoppers, *X*, serve to insulate pipe *M* from jacket *N*. The heated length is measured between the inner faces of the stoppers. A $^1/_4$-inch copper tube conducts the condensate out of the lowest point of the inner jacket to a mercury seal (not shown), which is immersed in an ice bath.

The outer steam jacket, *J*, consists merely of a short length of standard $3^1/_2$-inch iron pipe, closed by two standard pipe caps. The caps are drilled and tapped for $1^1/_2$-inch pipe so that the ends of the inner jacket may be screwed into them. The means of egress for the thermocouple wires and pressure leads, of steam admission, and of condensate withdrawal are obvious from the diagram. A small opening (not shown) in the right-hand pipe cap leads to a manometer for the measurement of steam pressure.

TABLE I. DIMENSIONS OF COPPER PIPE

	INCHES	CM.
Inside diameter	0.281	0.714
Outside diameter	0.405	1.029
Total length	66.0	167.6
Heated length	61.75	156.8
Unheated length at each end	2.13	5.4
Distance, inlet to thermocouples:		
A	0.63	1.6
B	3.0	7.6
C and *D*	33.0	83.8
E	63.0	160.0
Distance, inlet to pressure tap, *F*	5.0	12.7
Distance between pressure taps, *F* and *G*	56.0	142.2
Ratio, heated length to inside diameter	220	
Bakelite calming section:		
Inside diameter	0.281	0.714
Outside diameter	0.403	1.023
Length, runs 1–29	22.50	57.2
Length, runs 30–42	22.13	56.2

THERMOCOUPLES. The thermocouples on the wall of pipe *M* are junctions between No. 30 cotton-covered constantan wire and the metal of the tube, which serves as the second lead. The couples were attached by a method essentially that of Colburn and Hougen (*3*):

> A longitudinal slot 1 inch in length, and in width and depth equal to the diameter of the constantan wire, was cut in the surface of the copper. The insulation was removed from the tip of a piece of the wire, the cotton covering of which had been first impregnated with Bakelite varnish, and the wire was pressed into the slot. A drop of solder placed where the wire was bare formed the junction. Any excess of solder or projecting insulation was removed with fine emery cloth. In order to prevent the possible displacement of the thermocouples during the assembly of the apparatus, the insulated constantan wires were twisted once about the copper pipe at some distance from the junction. The thermocouples were calibrated in place.

AUXILIARY EQUIPMENT. The piping system by which the working fluid is delivered to and withdrawn from the test section is of brass or bronze, except for a short sight-glass by which suspended matter may be detected, and a calming-length of Bakelite tubing which precedes the copper pipe, *M*. The joints are made tight wherever necessary by solder or by

TABLE II. DATA AND CALCULATIONS OF RYNALSKI AND HUNTINGTON

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)	(14)	(15)	(16)	(17)	(18)[a]
				WALL TEMPERATURES													
RUN	W	t_1	t_2	T_A	T_B	T_C	T_D	T_E	T	q_S	q_G	$\frac{q_S - q_G}{q_S}$	$\frac{t_2 - t_1}{T - t_1}$	$\frac{Wc}{kL}$	$\frac{hd}{k}$	h	$\frac{dG}{\mu}$
	$\frac{Lbs.}{(Hr.)(Tube)}$	° C.	° C.	° C.	° C.	° C.	° C.	° C.	° C.	$\frac{B.t.u.}{Hr.}$	$\frac{B.t.u.}{Hr.}$	%				$\frac{B.t.u.}{(Ft.^2)(° F.)(Hr.)}$	
$T - t_1$ = 30° C. (approximately)																	
42	9.38	69.76	96.45	83.5	100.0	100.2	101.0	100.0	100.3	316	290	8.2	0.875	6.91	3.41	24.8	13.6
38	14.06	69.67	95.27	82.5	100.0	100.0	101.0	99.0	100.3	434	416	4.2	0.836	10.32	4.72	34.3	19.7
34	20.75	68.93	92.61	80.5	99.7	100.0	100.8	98.2	100.1	592	566	4.4	0.760	15.2	5.94	43.1	27.5
33	26.42	68.45	90.37	79.0	99.6	100.0	100.5	97.8	99.9	697	666	4.5	0.698	19.3	6.56	47.7	33.0
31	37.88	69.23	86.93	79.0	99.6	100.0	100.7	97.5	100.0	800	769	3.9	0.575	27.6	7.10	51.5	44.9
32	62.00	68.37	81.93	77.5	99.2	100.0	100.7	96.3	99.8	961	957	0.4	0.432	44.8	7.88	57.2	66.5
37	97.19	72.54	80.97	79.0	99.0	99.6	100.6	96.7	99.6	936	935	0.1	0.311	70.5	8.29	60.2	109.2
36	97.38	72.68	81.02	79.0	99.2	99.6	100.6	96.7	99.7	942	927	1.6	0.309	70.5	8.21	59.6	109.3
$T - t_1$ = 38° C.																	
26	36.13	62.03	84.63	74.5	99.7	100.1	100.0	97.6	99.9	960	926	3.5	0.596	26.2	7.09	51.2	35.4
$T - t_1$ = 45° C. (approximately)																	
22	60.19	54.73	74.93	65.0	98.6	99.0	99.6	94.5	98.9	1460	1353	7.3	0.457	42.9	8.08	58.2	41.0
23	65.75	54.10	74.24	65.0	98.6	99.9	99.5	95.0	99.2	1510	1470	2.6	0.446	46.9	8.59	61.8	43.5
24	66.00	54.07	74.23	64.5	97.7	98.8	99.2	94.7	98.4	1489	1478	0.7	0.455	47.0	8.81	63.5	43.7
$T - t_1$ = 65° C. (approximately)																	
8	10.54	34.35	94.48	60.5	100.0	100.5	100.0	96.8	100.1	753	704	6.5	0.915	7.52	4.03	29.0	7.2
19	13.75	36.70	92.70	61.0	99.9	100.6	100.5	98.0	100.3	887	857	3.4	0.880	9.81	4.91	35.4	9.4
18	13.88	36.23	92.68	60.5	99.6	100.3	100.3	97.7	100.0	904	871	3.6	0.885	9.88	5.00	36.0	9.5
9	17.90	34.90	90.90	58.0	99.6	100.3	99.9	96.5	99.9	1137	1112	2.2	0.861	12.72	6.12	44.1	11.2
17	19.88	35.51	88.76	57.5	98.8	99.6	98.7	95.6	99.0	1198	1172	2.2	0.839	14.12	6.48	46.6	12.1
7	25.50	31.83	84.93	52.5	98.8	100.2	99.6	96.1	99.4	1540	1487	3.4	0.785	18.01	7.42	53.2	12.7
6	29.00	31.15	83.00	51.5	98.8	100.1	99.6	96.5	99.4	1667	1643	1.4	0.761	20.4	7.95	57.0	13.6
41	29.25	34.93	83.03	55.5	98.7	99.5	100.1	96.0	99.3	1571	1548	1.5	0.747	20.7	7.85	56.3	15.3
10	35.00	33.80	79.10	52.5	98.7	100.0	99.2	94.7	99.2	1728	1733	−0.3	0.693	24.6	8.31	59.6	15.8
14	40.50	34.90	75.77	53.5	99.0	100.5	99.2	94.4	99.4	1814	1802	0.7	0.634	28.5	8.41	60.2	17.2
13	41.25	34.60	75.33	53.5	99.1	100.4	99.2	94.5	99.5	1834	1831	0.2	0.628	29.0	8.45	60.5	17.2
12	42.50	33.43	74.50	50.0	97.3	98.7	97.3	92.5	97.7	1898	1895	0.2	0.639	29.8	8.90	63.7	17.4
11	45.50	32.57	72.80	49.0	97.0	98.7	97.6	92.1	97.6	1960	1985	−1.3	0.619	31.8	9.07	64.9	16.8
16	62.81	33.73	65.87	50.0	98.6	100.1	98.9	92.1	99.1	2144	2174	−1.4	0.492	43.8	9.09	64.8	20.2
15	63.19	33.82	65.88	50.0	98.6	100.2	98.9	92.1	99.1	2128	2181	−2.5	0.491	44.0	9.11	65.0	20.3
40	80.44	35.41	61.72	50.0	97.5	99.0	99.9	92.0	98.5	2270	2276	−0.3	0.417	55.9	9.38	66.9	24.4
39	80.72	35.28	61.36	50.0	97.5	99.0	100.0	92.0	98.5	2290	2263	1.2	0.413	56.2	9.30	66.3	24.5

[a] μ taken at $^1/_2\,(t_1 + t_2)$ for 95 per cent glycerol from tables of L. V. Cocks, *J. Soc. Chem. Ind.*, **48**, 279T (1929), who gives, for example, $\mu_{50} = 0.64$, $\mu_{70} = 0.27$, $\mu_{90} = 0.12$, $\mu_{100} = 0.084$, where the subscript gives temperature in ° C. and viscosity unit is the poise.

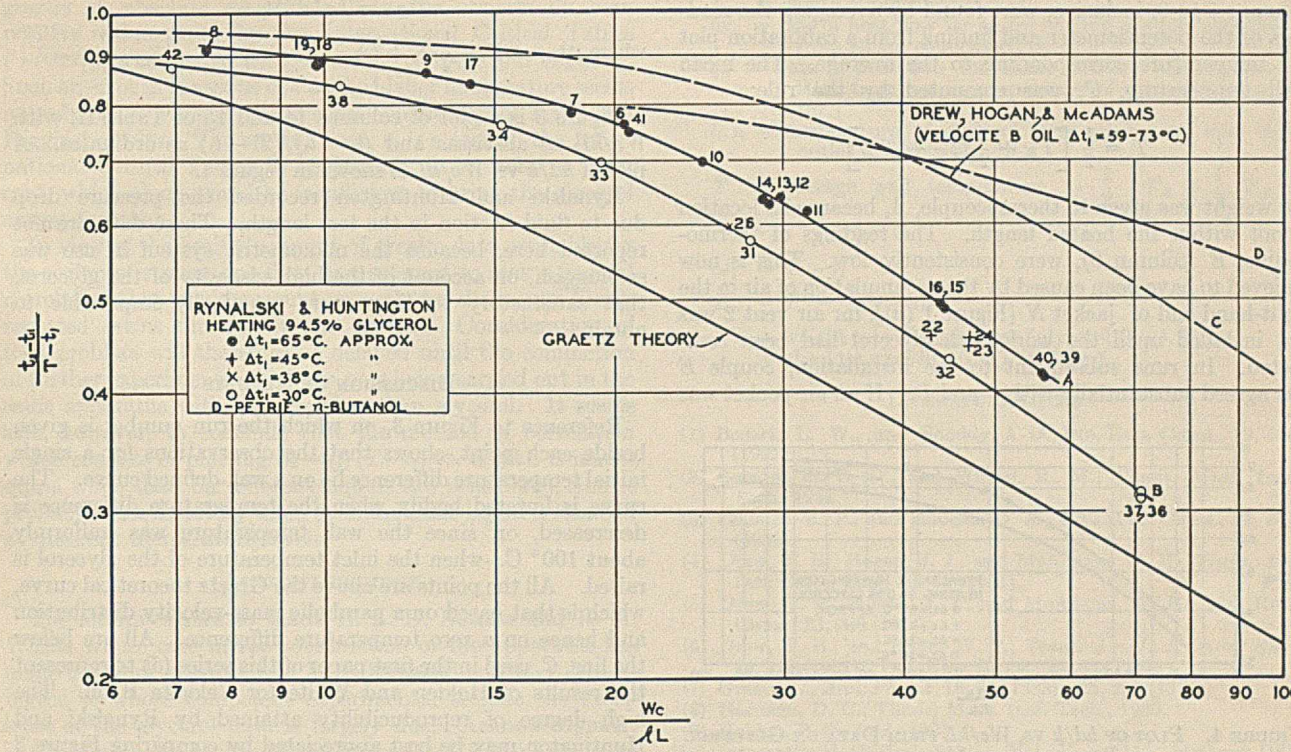

FIGURE 3. PLOT OF *Wc/kL* VS. (TEMPERATURE RISE/INITIAL TEMPERATURE DIFFERENCE) FOR GLYCEROL AT SEVERAL INLET TEMPERATURES

Wall temperature is about 100° C.

a talc–sodium silicate cement. Progressive contamination of the heating surface has been so far reduced by using these materials of construction that cleaning of the copper pipe, although retained as a regular procedure, is almost unnecessary.

The Bakelite calming section is insulated by a vacuum jacket and buried in a box of loose magnesia lagging.

The calibrated mercury thermometer at the inlet of the calming section, as well as that at the outlet of the copper pipe, is preceded by a motor-driven stirrer of variable speed. In experiments on glycerol, without steam in the jacket, no measurable rise in temperature of the working fluid was occasioned by the stirrers.

In other respects the external equipment embodies no unusual features. The liquid under test may be either circulated through a calibrated orifice for measurement or discharged into a weighing tank. Suitable preheaters and coolers are, of course, included.

Figure 2 is a photograph of the assembled apparatus.

EXPERIMENTS WITH GLYCEROL

WORKING FLUID. The glycerol used by Rynalski and Huntington in securing the following data was commercial C. P. glycerol.[2] The apparent specific gravity (25°/25° C.) was initially 1.2488, as determined with a Geissler pycnometer. This corresponds to a water content of 5.12 per cent (*1*). A measurement of the refractive index gave an identical result for the water content. After twenty-nine runs, sufficient water had been picked up from the atmosphere to raise the percentage to 5.75. At this point enough new glycerol was added to reduce the water content to 5.55 per cent. At the end of the experiments the amount of water present was 5.74 per cent. These slight variations in concentration had no discernible influence on the results.

OPERATION. The heating medium in all the tests was slightly superheated (0.5° to 1° C.) steam which was delivered to the steam jacket at such a rate that the pressure maintained therein was approximately 1 inch of water above atmospheric. The rate of flow of glycerol was determined by weighing the total quantity of liquid discharged during a given run. The runs varied in length from 20 minutes to 2 hours. A Leeds and Northrup portable potentiometer was used to read the thermocouples. The copper pipe was cleaned after runs 12, 19, and 29.

TABLE III. BLANK RUNS WITH NO FLOW OF GLYCEROL

RUN	CONDENSATE FROM INNER JACKET *N* *Grams/hour*	
20	3.63	Without vacuum jacket on calming section
21	3.56	
30	0.94	With vacuum jacket

DATA AND COMPUTATIONS. In all, forty-two runs were made; they are numbered in chronological order. Of these, twenty-nine are listed in Table II; and three "blanks," runs 20, 21, and 30, during which there was no flow of glycerol, are shown in Table III. Runs 1 to 5, inclusive, were merely preliminary tests; the data for them are either incomplete or known to be erroneous in some particular. The operating conditions during runs 25, 27, and 35 fluctuated so widely that precise measurements were impossible; hence these runs are not reported. Runs 28 and 29 are omitted because they were made with a high inlet temperature (82° C.) and at low rates of flow, prior to the installation of the vacuum jacket on the calming section. This jacket was used in runs subsequent to and including the thirtieth.

The runs tabulated in Table II are given, for each inlet temperature level, in order of increasing mass velocity. The temperatures in columns 3 to 9, inclusive, are arithmetic averages of from three to seventeen readings, depending on the length of the run. The wall temperatures reported in

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[2] Supplied by Lever Brothers, Cambridge, Mass.

columns 5 to 9, inclusive, were found by averaging the readings of the potentiometer and finding from a calibration plot the temperature corresponding to the average. The mean wall temperature, T, was computed by the rule:

$$T = \frac{1}{2}\left[T_B + \frac{1}{2}(T_C + T_D)\right]$$

No weight was given to thermocouple, A, because its location is not within the heated length. The readings of thermocouple, E (column 9), were consistently low. This is now believed to have been caused by the accumulation of air in the right-hand end of jacket N [Figure 1 (a)], for air vent 2 was not installed until the work with glycerol had been completed. In runs subsequent to the installation, couple E has agreed substantially with C and D. If an air pocket was truly the cause of the low readings so that the surface temperature was actually as recorded, by referring to Figure 1 (a) it appears that a maximum of one-sixth of the length of the heating surface might have been at the relatively low temperature listed in column 9. An average T, computed by giving T_B a weight of one-sixth, differs but slightly from the value found by the rule used.

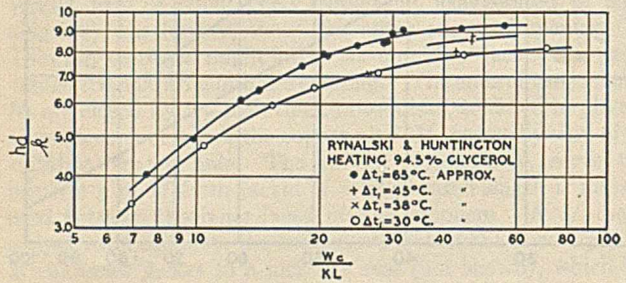

FIGURE 4. PLOT OF hd/k VS. Wc/kL FROM DATA ON GLYCEROL BY RYNALSKI AND HUNTINGTON

h is based on an arithmetic mean, Δt

The heat, q_S, given up by the steam to pipe M is calculated from the weight of condensate in the inner jacket, N, after subtracting the condensate collected in the blanks. The correction, which is almost negligible, was taken as 3.6 grams per hour in runs 6 to 29; and as 0.9 gram per hour in the later runs (Table III).

The specific heats, c, used in computing the values of Wc/kL in column 15, as well as in obtaining the heat picked up by the glycerol, are taken from the values given for 100 per cent glycerol by the International Critical Tables (*10*). It is possible that these values are slightly too low for the 94.5 per cent glycerol used by Rynalski and Huntington. However an estimated correction (doubtful at best) was found to be less than the probable error reported for the data on the pure liquid at the temperatures involved (40–80° C.). The value of c used in the calculations was taken at the arithmetic mean of the terminal temperatures of the fluid.

In finding the quantities Wc/kL and hd/k, the values of k employed were those found by Kaye and Higgins in 1928 (*11*):

$$k_t = 0.163\ (1 + 0.00053t)\ \frac{\text{B. t. u.}}{(\text{ft.})(\text{hr.})(°\text{ F.})}$$

where t = Centigrade temperature

At the higher temperatures (80° C.) the figures reported in the International Critical Tables are 18 per cent greater than the results of Kaye and Higgins, and are believed to be of inferior accuracy. The "density" of Kaye and Higgins' glycerol was 1.25 at 18° C. As in the case of the specific heat, the value of k was taken at the average fluid temperature.

The coefficient of heat transfer, h, which occurs in the quantity hd/k of column 16 is defined by the relation—

$$q_G = h\pi Ld\ \Delta t_{\text{av.}}$$

where $\Delta t_{\text{av.}} = T - \frac{1}{2}(t_2 + t_1)$

Figure 3 is a plot of columns 14 and 15 of Table II, with Wc/kL as abscissas and $(t_2 - t_1)/(T - t_1)$ as ordinates. A plot of hd/k vs. Wc/kL is shown in Figure 4.

Rynalski and Huntington recorded the pressure drop due to fluid friction in the test length. These data are not reported here, because the manometric system in use was so sluggish, on account of the high viscosity of the glycerol, that satisfactory readings were practically impossible to obtain.

DISCUSSION OF RESULTS

Reference to Figure 3, on which the run number is given beside each point, shows that the observations for a single initial temperature difference lie on a well-defined curve. The curve is lowered bodily when the temperature difference is descreased, or, since the wall temperature was uniformly about 100° C., when the inlet temperature of the glycerol is raised. All the points are above the Graetz theoretical curve, which is that based on a parabolic mass-velocity distribution and hence on a zero temperature difference. All are below the line, C, used in the first paper of this series (*5*) to represent the results of Holden and White for Velocite B oil. The high degree of reproducibility attained by Rynalski and Huntington may be best appreciated by comparing Figure 3 of this paper with Figure 1 of the earlier article (*5*), at the same time remembering that the present plot is drawn to a scale between two and three times as large as was the earlier graph.

The vertical spread between the two curves, A and B, varies from about 5 per cent at the extreme left of Figure 3, to 13 per cent at the right. This deviation would be almost within the experimental error for all data heretofore available. The horizontal spread varies from 50 per cent for small values of Wc/kL to about 20 per cent for large values. If the data were to be recalculated, using the value of $t_2 - t_1$ computed from the weight of steam condensed instead of using the directly measured rise in fluid temperature, both curves in Figure 3 would be raised slightly by an amount that decreases as Wc/kL increases (Table II, column 13). However, the possible correction is practically the same in magnitude and direction for each curve at those values of Wc/kL where the shift would be appreciable; hence the effect of the change in basis would be merely to make the curves A and B more nearly tangent to C at small values of Wc/kL without causing a substantial alteration in the spread. Somewhat similarly, the result of changing, in any reasonable manner, the chosen method of finding the average wall temperature, T, would be to shift both curves simultaneously in the same direction without reducing the spread appreciably. This would occur because the wall-temperature distributions are similar for the various runs. The measurement most likely to be erroneous is that of the wall temperature. Even if that determination is supposed doubtful by the improbably gross amount of ±1° C., the ordinate of a given point would be altered by only about ±4 per cent in the worst case.

From these considerations it appears that the deviations between the sets of data for the different inlet temperatures are considerably beyond the experimental error of the present work, unless it be supposed that the specific heat, c, and thermal conductivity, k, are grossly incorrect. In the case of the latter physical property there may be some doubt as to the accuracy of the values chosen, as pointed out previously. To bring curves A and B together would require that the coefficient of temperature variation of k be negative and greater in absolute magnitude than the abnormally high positive value given by the International Critical Tables (+0.0026 as compared with +0.00053 of Kaye and Higgins). Such an error in the value of k at the higher temperature seems improbable in view of the general consistency of Kaye and Higgins' results. The specific heat, c, is stated in the International Critical Tables to be possibly in error by ±5 per cent, which alone would be insufficient to bring the glycerol curves together.

In view of the limited amount of precise data available for the region of stream-line flow, any attempt to seek a general correlation that would account properly for the results herein reported seems unwise for the present. Consideration of that problem will therefore be delayed until the completion of further experiments which are now being carried out in the same apparatus with liquids other than glycerol. It seems safe, however, to conclude that the method of correlation which consists of plotting $(t_2-t_1)/(T-t_1)$ vs. Wc/kL is inadequate when data on different liquids are considered, and is probably unsatisfactory when even the same liquid is handled at different temperature levels.

ACKNOWLEDGMENT

The author wishes to thank H. S. D. Botzow and R. M. Wilson whose care in the construction of the apparatus has made the work possible, and A. T. Rynalski and R. L. Huntington to whose competent experimental technic the excellence of the glycerol data is largely due. Acknowledgment is also due to W. H. McAdams for his constructive criticism and assistance in the direction of this investigation.

NOMENCLATURE

c = heat capacity, (B. t. u.)/(lb.)(° F.), taken at $t_{av.} = \frac{1}{2}(t_1 + t_2)$
d = inside diameter of pipe, feet
G = mass velocity, lbs./(ft.²)(hr.) = $4W/\pi d^2$
h = coefficient of heat transfer, $\frac{\text{(B. t. u.)}}{\text{(hr.)(ft.}^2\text{)(° F.)}}$
k = thermal conductivity, $\frac{\text{B. t. u.}}{\text{(hr.)(ft.}^2\text{)(° F./ft.)}}$, taken at $t_{av.} = \frac{1}{2}(t_1 + t_2)$
L = length of pipe heated, feet
q_S = rate of heat flow for entire heating surface, calculated from steam condensed, (B. t. u.)/(hr.)
q_G = rate of heat flow for entire heating surface, calculated from rise in temperature of glycerol (B. t. u.)/(hr.)
t_1, t_2 = temperature of glycerol after mixing at inlet and outlet, respectively, ° C.
T = average wall temperature = $\frac{1}{2}\left[T_B + \frac{1}{2}(T_C + T_D)\right]$, ° C.
$\Delta t_1 = T - t_1$
$\Delta t_{av.} = T - \frac{1}{2}(t_2 + t_1)$
W = weight rate of discharge of glycerol (lbs.)/(hr.)
μ = absolute viscosity (lbs.)/(ft.)(hr.)

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Rudolph II, Emperor of Germany, in the Laboratory of His Alchymist, 1576

By Vacslaw Brozik

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Linseed Oil

Changes in Physical and Chemical Properties during Heat-Bodying

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THE CHANGES in certain physical and chemical properties of heat-bodied linseed oil during processing at different temperatures have been observed. The properties studied are viscosity, color, specific gravity, apparent mean molecular weight, index of refraction, acid value, and iodine value. These were measured on samples withdrawn from commercial batches (250 gallons) during bodying. The results are presented in connection with the time-rate of change of each property, as well as the rate of change of each property with respect to the others.

IT IS generally known that, in the process of bodying linseed oil from its raw state to that of a heavy viscous liquid, many changes, both physical and chemical, are taking place concurrently. While the exact program of these changes is not known, nor all the factors that affect their speed and sequence, it is agreed that reactions of polymerization, condensation, cracking, oxidation, hydrolysis, rearrangement, and gelation are involved.

It seemed of interest to ascertain at what rate these changes took place at different temperatures, and, if possible, what interrelations could be discovered among them. The authors are aware of the fact that separate studies of the changes of individual properties have been made by different investigators on different oils under controlled laboratory conditions, but it seemed worth while to study these changes as they occurred in oils bodied on a commercial scale, notwithstanding the fact that experimental conditions cannot be so accurately controlled as in small-scale operations. For the first runs, two 250-gallon monel-metal kettles, heated by means of fuel oil over a free fire, were filled with neutral oil and heated to 327.7° C. (622° F.) and 307.2° C. (585° F.), respectively. Later three similar kettles of oil were heated to the following maximum temperatures: 287.8° C. (550° F.), 304.4° C. (580° F.), and 329.6° C. (625° F.). The first kettle (327.7° C.) was on the fire for 2$^1/_2$ hours, the second (307.2° C.) for 9$^1/_2$ hours, the third (329.6° C.) for 3 hours, the fourth (304.4° C.) for 6 hours, and the fifth (287.8° C.) for 22 hours, inclusive of the time necessary to raise to the maximum temperature. There was no increase in temperature when any kettle was taken off the fire, because during the processing the burners were adjusted as the temperature of the kettle rose or fell. The times necessary to reach the maximum temperatures and the complete record of the changes in properties which were measured are shown in Tables I, II, and III, and in the figures that are presented below.

Determination of Properties

The oil used was an alkali-refined (neutral) oil which had the following characteristics:

	First Two Kettles	Last Three Kettles
Color	6	6
Specific gravity at 15.5° C.	0.9321	0.9242
Molecular weight	700	793
Index of refraction	1.4769	1.4800
Acid value	0.402	0.445
Iodine value	180.3	179.3

During the period of bringing up to temperature, two 4-ounce samples were taken from each kettle every half-hour and thereafter every 15 minutes.

Color. The color value was obtained in the following way: One gram of potassium dichromate was dissolved in 100 cc. concentrated sulfuric acid (specific gravity 1.86). The number of cubic centimeters of this solution which it is necessary to add to 100 cc. of colorless concentrated sulfuric acid to match the tint of the oil is called the color value.

Specific Gravity. A Westphal balance was employed, and the results were recalculated to specific gravities at 15.5° C. in terms of water at 4° C., using the following data from Fritz (*2*), giving fractional increase in specific gravity per degree fall in temperature:

22.8° to 170° C.	0.0006707
170° to 226° C.	0.0006857
226° to 243° C.	0.0006877

Molecular Weight. The freezing-point depression method of Beckmann was employed to give the apparent mean molecular weight. Nitrobenzene was used as solvent

Objection may be made, and rightly, to the use of this

Table I. Physical and Chemical Constants of Bodied Linseed Oil

	Oil Bodied at 327.8° C.					Oil Bodied at 307.2° C.				
Time	Temp. ° C.	Refractive index	Acid value	Mol. weight	Sp. gr.	Temp. ° C.	Refractive index	Acid value	Mol. weight	Sp. gr.
7:45	27	1.4769	...	700	....	27	1.4769	..	700	....
8:00	135	1.4775	0.40	..	0.9340	116	1.4771	0.31	..	0.9321
8:30	216	1.4778	0.60	..	....	171	1.4771	..	..	0.9333
9:00	293	1.4782	0.93	830	0.9365	238	1.4771	0.44	753	0.9340
9:30	325	1.4790	2.79	..	0.9402	291	1.4775	..	..	0.9346
10:00	327.8	1.4832	8.54	913	0.9569	302	1.4784	1.39	..	0.9371
10:30	325	1.4851	12.21	..	0.9655	303	1.4792	..	..	0.9402
11:00	315	1.4867	14.78	1600	0.9695	307	1.4805	3.22	795	0.9434
11:30	299	1.4871	...	1678	0.9702	307	1.4816	..	..	0.9453
12:45	249	....	...	..	....	302	....	..	..	....
1:00	246	1.4871	15.13	1620	0.9682	303	1.4829	5.29	883	0.9563
1:30	229	1.4871	...	..	....	307	1.4835	..	..	....
2:00	221	1.4871	15.10	1565	....	306	1.4843	6.61	1220	....
2:30	210	1.4871	...	..	0.9695	305	1.4850	..	..	0.9629
3:00	190	1.4870	14.83	..	....	288	1.4852	7.28	1250	0.9642
3:30	185	....	...	..	....	279	1.4855	..	..	....
4:00	176	....	15.10	..	....	306	1.4858	7.77	1480	....
4:30	112	1.4870	14.80	1602	0.9702	302	1.4861	8.00	..	0.9669
24 hours later	...	....	...	1608	....	..	....	..	1542	....

Table II. Physical and Chemical Constants of Bodied Linseed Oil

Time	Oil Bodied at 329.4° C.								Oil Boiled at 304.4° C.								Oil Bodied at 287.7° C.							
	Temp. ° C.	Acid value	Iodine value	Viscosity Poises	Sp. gr.	Mol. weight	Refractive index	Color	Temp. ° C.	Acid value	Iodine value	Viscosity Poises	Sp. gr.	Mol. weight	Refractive index	Color	Temp. ° C.	Acid value	Iodine value	Viscosity Poises	Sp. gr.	Mol. weight	Refractive index	Color
8:00 A. M.	32	0.45	179.5	...	0.9245	785	1.4800	6	32	0.60	179.3	...	0.9242	803	1.4800	6	32	0.73	179.2	..	....	..	1.4800	6
8:15	...	...	...	...	....	..	....	...	...	..	...	...	....	..	....	...	...	..	...	..	....	..	....	...
8:30	93	0.55	...	...	0.9225	..	1.4800	5.5	93	0.56	...	...	0.9246	..	1.4800	6	93	..	...	..	....	..	....	...
8:45	...	...	...	...	....	..	....	...	...	..	...	...	....	..	....	...	...	..	...	..	....	..	....	...
9:00	179	0.55	179.2	...	0.9252	808	1.4801	5.5	168	0.54	179.7	0.50	0.9257	792	1.4802	6	168	..	179.3	..	0.9253	787	1.4798	6
9:15	...	...	...	0.50	....	..	....	...	...	..	...	...	....	..	....	...	...	..	...	..	....	..	....	...
9:30	249	0.62	172.3	0.50	0.9316	..	1.4805	2.5	241	0.66	...	0.50	0.9281	..	1.4808	4.5	213	..	...	..	0.9254	..	1.4805	5.5
9:45	282	1.08	...	0.65	....	..	1.4810	...	...	..	...	...	....	..	....	...	...	..	...	..	....	..	....	...
10:00	313	2.04	166.2	0.75	0.9343	860	1.4812	1.5	304	1.78	167.1	0.70	0.9258	810	1.4810	2.5	271	1.06	176.0	0.50	0.9254	821	1.4807	2.5
10:15	321	3.19	160.1	1.40	....	851	1.4820	...	...	..	...	...	....	..	....	...	...	..	...	..	....	..	....	...
10:30	327	5.12	149.8	2.12	0.9402	951	1.4835	1	307	2.62	...	1.00	0.9324	826	1.4815	1.5	291	..	...	0.65	0.9262	..	1.4810	1.5
10:45	327	...	143.5	5.90	....	1079	1.4854	...	307	..	...	1.06	....	893	1.4823	...	...	..	...	..	....	..	....	...
11:00[a]	329	9.79	139.9	10.80	0.9511	1217	1.4870	2.5	304	3.46	153.5	1.46	0.9374	928	1.4828	1.5	288	1.86	167.1	0.92	0.9273	848	1.4816	1
11:15	324	11.83	136.6	16.71	....	1253	1.4880	5.5	302	..	...	1.71	....	..	1.4834	...	291	..	...	..	....	..	....	...
11:30	316	13.36	129.5	20.1	0.9513	1323	1.4886	6	299	4.41	...	2.12	0.9413	..	1.4840	1.5	291	..	...	..	....	..	....	...
11:45	310	13.98	126.3	21.0	....	1409	1.4890	6.5	299	..	...	2.37	....	..	1.4842	...	291	..	...	..	....	..	....	...
12:00 M.	304	14.63	...	27.0	0.9525	..	1.4893	7	296	4.67	144.8	3.20	0.9440	1002	1.4850	1.5	288	2.55	158.3	1.12	0.9338	881	1.4823	1
12:15 P. M.	296	...	...	...	....	..	1.4893	...	302	..	...	...	....	..	1.4849	...	291	..	...	..	....	..	....	...
12:30	285	14.69	...	...	....	..	1.4897	...	299	5.57	...	4.09	0.9465	..	1.4852	1.5	291	..	...	..	....	..	....	...
12:45	277	...	127.9	28.4	....	1520	1.4897	...	302	..	...	4.35	....	..	1.4857	...	291	..	...	..	....	..	....	...
1:00	268	14.61	...	...	0.9546	..	1.4900	7	304	6.12	143.6	...	0.9506	1122	1.4860	1.5	285	3.19	148.3	1.76	0.9383	939	1.4835	1
1:15	260	...	...	36.2	....	..	1.4900	...	302	..	...	5.50	....	..	1.4862	...	291	..	...	..	....	..	....	...
1:30	252	14.65	...	37.6	0.9561	..	1.4899	...	304	6.52	...	6.27	0.9530	..	1.4865	1.5	291	..	...	..	....	..	....	...
1:45	246	...	...	39.0	....	..	1.4900	...	299	..	...	6.75	....	..	1.4867	...	288	..	...	..	....	..	....	...
2:00	238	14.48	127.3	...	....	1563	....	7	299	6.97	138.2	8.84	0.9552	1304	1.4871	2	295	3.86	142.9	2.75	0.9408	989	1.4846	1
2:15	229	...	128.2	40.4	....	1562	....	...	[a]	..	...	9.07	....	..	1.4873	...	288	..	...	..	....	..	....	...
2:30	224	14.24	...	...	0.9571	..	1.4900	...	293	7.56	...	9.77	0.9563	..	1.4878	2	287	..	...	..	....	..	....	...
2:45	218	...	...	...	....	..	....	...	288	..	...	10.70	....	..	1.4876	...	288	..	...	..	....	..	....	...
3:00	210	...	128.3	...	0.9608	1513	1.4900	7	277	7.74	135.0	12.48	0.9567	1298	1.4880	2	288	4.41	141.1	3.55	0.9432	1041	1.4853	1
3:15	204	...	...	...	....	..	....	...	271	..	...	...	....	..	1.4880	...	293	..	...	..	....	..	....	...
3:30	199	14.17	...	...	0.9603	1525	....	...	263	7.43	...	12.58	0.9598	..	....	2	291	..	...	..	....	..	....	...
3:45	193	...	...	...	....	..	....	...	254	..	...	...	....	..	1.4880	...	291	..	...	..	....	..	....	...
4:00	188	14.25	127.9	...	0.9619	1535	1.4900	8	246	7.45	135.4	12.90	0.9595	1373	....	2	288	4.78	141.6	4.90	0.9476	1066	1.4860	1
4:15	185	...	...	...	....	..	....	...	241	..	...	...	....	..	....	...	285	..	...	..	....	..	....	...
4:30	179	14.25	...	...	0.9636	..	1.4900	...	232	7.46	...	12.90	0.9550	1365	1.4880	...	288	..	...	..	....	..	....	...
4:45	174	...	...	...	....	..	....	...	227	..	...	12.90	....	..	....	...	291	..	...	..	....	..	....	...
5:00	171	14.14	125.8	...	0.9632	1594	1.4900	8.5	221	7.33	132.9	...	0.9534	1282	1.4880	2	288	5.35	134.9	7.01	0.9520	1132	....	2
Next day 8:00 A. M.	...	14.13	126.7	...	0.9627	1602	1.4900	8.5	...	7.36	130.0	...	0.9552	1281	1.4880	2	...	..	...	..	....	..	....	...

[a] Time kettle was taken off fire.

solvent in molecular-weight determinations on oils, for free fatty acids are polymerized to some extent in solution (*4*), but it is not believed that glycerides are. The authors are sure that the results show the true trend of change in molecular-weight values during processing, but admit that the results are more in error where greater hydrolysis has taken place, that is, toward the end of the heating.

INDEX OF REFRACTION. The Abbé instrument was used and the determinations were made at 21° C.

VISCOSITY. These values are expressed in poises and were obtained with the Gardner-Holt bubble viscometer at 25° ± 1° C.

ACID VALUE. These were obtained by refluxing a mixture of approximately 10 grams of oil with 50 cc. of an equal-volume mixture of benzene and 95 per cent ethyl alcohol on the water bath for 30 minutes, cooling, and titrating with alcoholic potassium hydroxide, using phenolphthalein as indicator.

Some acid values in this and other solvents were determined by potentiometric titration, using the quinhydrone electrode and saturated alcoholic lithium chloride–calomel half-cell. The results of this study have been presented in another paper (*1*).

IODINE VALUE. The Hanus method was used and the determinations were made in a dark chamber at 23° ± 2° C. for 1 hour.

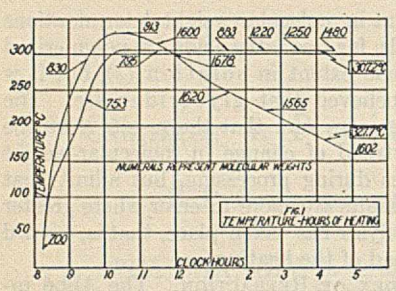
RESULTS

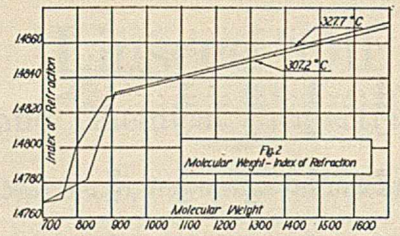
Table I gives the time, temperature, specific gravity, index of refraction, molecular weight, and acid value for samples withdrawn from the first two batches of oil during bodying.

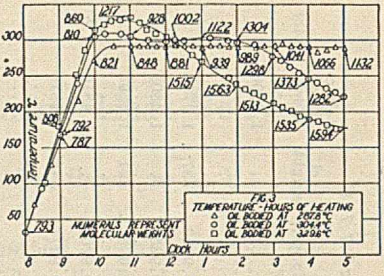
Figure 1 shows the time–rate of change of temperature, and the molecular weights of the oil samples at certain times during the bodying are also indicated.

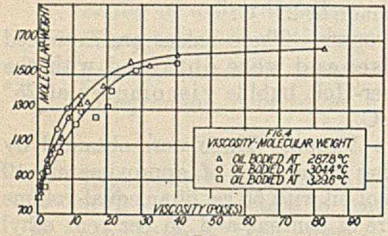
It will be noticed that in the case of the 327.7° C. (622° F.) oil, although the molecular weight changes by only 200 units during the 2 hours of bringing up to maximum temperature, during the next hour there is an increase of 687 units in molecular weight, notwithstanding the fact that the oil is cooling. There is also some indication of slight depolymerization on cooling in the last stage.

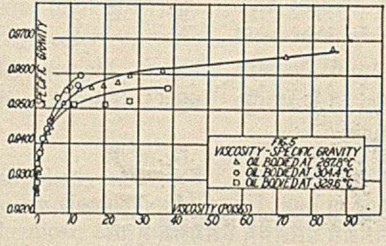
The temperature of the other kettle, 307.2° C. (585° F.), was maintained more constant after the maximum had been reached. There is an increase of less than 200 units in molecular weight during the first 5 hours of heating; but between the fifth and sixth hours there is a sudden increase of 337 units, and this increase continues slowly for the rest of the run, reaching a final value over twice as great as the initial one, and approximately equal to the value reached in the oil heated to the higher temperature.

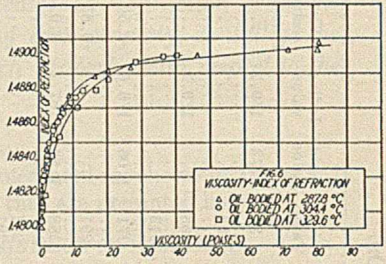


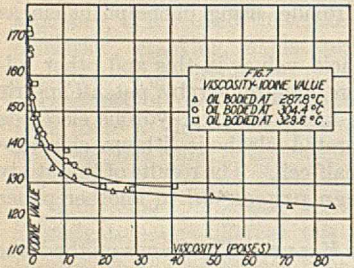












As might be expected, the higher the temperature the more sudden the increase in index of refraction. For example, the high-temperature oil undergoes approximately the same increase in 3 hours as the low-temperature oil experiences in 9 hours.

A graph of indices of refraction against molecular weights for these oils (Figure 2) shows that, during the first stages of bodying, the refractive index increases considerably with correspondingly small increase of molecular weight, while during the latter part of processing, the increase in molecular weight is large, with correspondingly small increase in refractive index. The turning point, which is quite marked, comes for the high-temperature oil when the molecular weight has reached a value of 915, for the lower-temperature oil when the molecular weight is 885, and the curves for both oils closely approximate each other. Evidently molecular rearrangements take place during the heating to some extent before polymerization reactions set in. It may also be noted that at this turning point (molecular weight around 900, refractive index around 1.483 for both oils) the viscosities differ by only one-half bubble when tested in the 10.75-mm. Gardner-Holt tube, the higher-temperature oil being the heavier.

The experimental results for the latter three oils are, perhaps, more dependable. These are exhibited in Table II, which gives time, temperature, specific gravity, color, index of refraction, mean molecular weight, viscosity, acid value, and iodine value.

Figure 3 gives the temperature-time relations for the three oils. Upon the curves have been indicated the molecular-weight values at corresponding times. The rate at which the oils were brought up to their maximum temperatures was the same for all. The 329.6° C. (625° F.) oil was permitted to cool after reaching maximum temperature; the 304.4° C. (580° F.) oil was kept on the fire 4 hours after reaching maximum temperature and then permitted to cool; the 287.8° C. (550° F.) oil was kept at maximun temperature without fluctuation for the remainder of the run, which continued for a day and a half longer than with the other two oils.

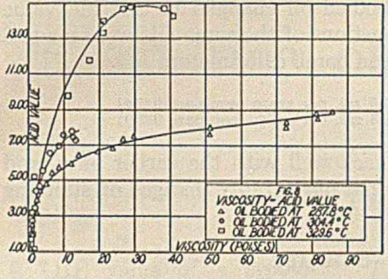
The same sudden increase in molecular-weight values during a short period of time such as was noted with the former oils is again seen, especially in the case of the high-temperature oil.

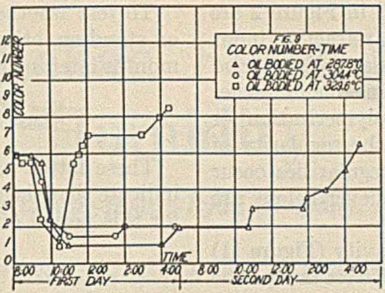
In connection with any discussion of the changes in properties which proceed during bodying, it must not be forgotten that the system is a complex one; that different reactions are possible and are going on concurrently; and that the results of the present, or of any single, investigation must be influenced by local conditions (methods of heating, shape and

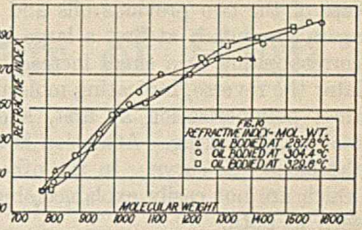
Table III. PHYSICAL AND CHEMICAL CONSTANTS OF BODIED LINSEED OIL

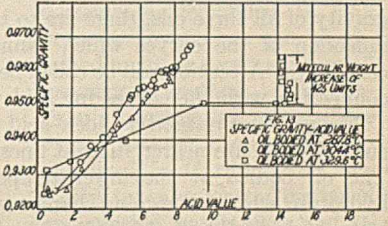
(Oil bodied at 287.8° C. for additional 1½ days)

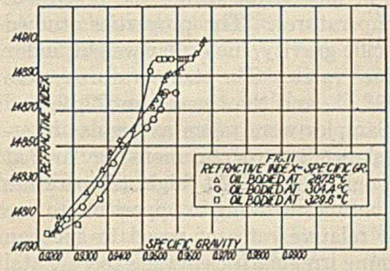
TIME	TEMP. ° C.	ACID VALUE	IODINE VALUE	VISCOSITY Poises	SP. GR.	MOL. WEIGHT	REFRACTIVE INDEX	COLOR
8:00 A. M.	38	5.31	134.4	...	0.9525	..	1.4870	2
9:00	127	..	...	...	....	..	....	...
9:15	177	..	...	...	....	..	....	...
9:30	229	..	...	...	....	..	....	...
9:45	274	..	...	...	....	..	....	...
10:00	291	5.59	...	...	0.9533	..	1.4873	2
10:15	288	5.70	132.7	9.07	....	1251	....	...
10:30	291	..	...	9.46	0.9536	..	1.4877	2
10:45	291	..	...	10.08	....	..	....	2
11:00	288	5.98	131.4	12.27	0.9549	1330	1.4880	2
11:15	288	..	...	...	....	..	....	2
11:30	288	..	...	12.90	0.9555	..	1.4880	2
11:45	288	..	...	13.57	....	..	....	2
12:00 M.	279	6.31	130.2	14.14	0.9552	1336	1.4882	3
12:15 P. M.	291	..	...	...	....	..	....	...
12:30	285	..	...	16.36	0.9560	..	1.4888	3
12:45	291	..	...	16.71	....	..	....	...
1:00	285	6.63	131.5	18.88	0.9560	1433	1.4887	3
1:15	288	..	...	19.30	....	..	....	...
1:30	288	..	...	20.10	0.9566	..	1.4890	3
1:45	285	..	...	21.00	....	..	....	...
2:00	287	6.85	127.9	23.56	0.9575	..	1.4891	3
2:15	285	..	...	...	....	..	....	...
2:30	288	..	...	23.80	0.9597	..	1.4890	3
2:45	288	..	...	24.42	....	..	....	3
3:00	288	7.24	127.7	27.00	0.9597	1568	1.4892	3.5
3:15	288	..	...	...	....	..	....	...
3:30	288	..	...	...	0.9609	..	1.4894	...
3:45	288	..	...	30.1	....	..	....	...
4:00	288	7.52	126.1	...	0.9602	1545	1.4898	4
4:15	288	..	...	34.7	....	..	....	...
4:30	285	..	...	36.20	0.9610	..	1.4899	...
4:45	288	..	...	36.20	....	..	....	...
5:00	288	7.84	127.8	...	0.9610	1610	1.4900	5
8:00 A. M.	36	7.69	126.0	50.90	0.9610	..	1.4900	6
9:30	285	7.95	...	57.20	0.9603	..	1.4900	6
9:45	288	..	...	...	....	..	....	6
10:00	291	8.10	123.2	...	0.9610	..	1.4900	...
10:15	285	..	...	72.40	....	..	....	...
10:30	288	8.14	...	...	0.9625	..	1.4903	...
10:45	288	..	...	...	....	..	....	...
11:00	288	8.55	...	81.40	0.9649	..	1.4905	6.5
11:15	288	..	...	...	....	1657	....	...
11:30	287	8.75	...	...	0.9668	..	1.4907	...
11:45	286	..	...	...	....	..	....	...
12:00 M.	279	8.84	123.3	85.30	0.9671	..	1.4910	6.5

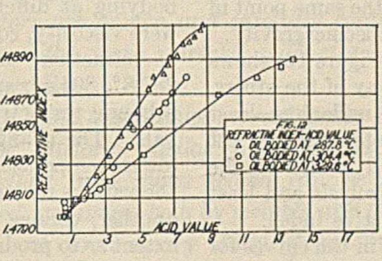


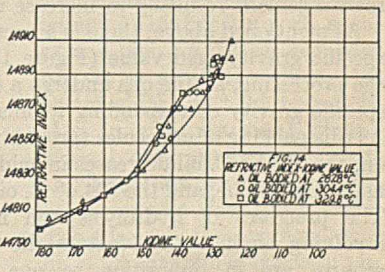












material of kettle, and effect of moisture formed by reactions or derived from the air).

Numbers are hard to visualize. The changes in properties with time are made more apparent when plotted. In a general way it may be observed that the changes experienced by the 287.8° C. (550° F.) oil are slower and more regular than those of the others. The slope of all the curves is gradual. The curves for the 304.4° C. (580° F.) oil are similar but steeper. With the 329.6° C. (625° F.) oil there is, in general, a sudden sharp increase in rate of change beginning during the second hour of heating and attaining a maximum during the third hour.

Viscosity means much to the practical paint-and-oil man. Figure 4 shows the relation of viscosity to molecular weight. There is no straight-line relationship. For all temperatures the increase in molecular weight is more rapid at first than in viscosity, but the viscosity increase preponderates later. In fact, in the 287.8° C. oil toward the end of the run, quite a large increase in viscosity is accompanied by only a small increase in molecular weight. Here, no doubt, gelation is going on—some sort of mechanical packing of the molecules which inhibits their free flow—but polymerization reactions are not proceeding to any extent.

It is of course true that a molecular weight determined in solution does not necessarily indicate the molecular weight of the substance in pure form; the solvent may exert a polymerizing or depolymerizing influence. In the present case the solvent has a polymerizing tendency.

The curves for viscosity–specific gravity (Figure 5) have the same form. This is to be expected. It is interesting to note at the end the large increase in viscosity accompanied by so small an increase in specific gravity. This ties up with the view that gelation is a process of enmeshing of molecules, and does not necessarily involve close packing, which would show itself in increased molecular weight, or specific gravity, or both.

The same is shown in the graph of viscosity–index of refraction (Figure 6). The behavior of the 304.4° C. (580° F.) and 287.8° C. (550° F.) oils is the same up to a certain point, possibly indicating that at first a certain program of changes must be gone through, irrespective of the temperature, provided the difference in temperature is not too great. The curve for the 329.6° C. (625° F.) oil goes its own course from the start, but coincides with the low-temperature curve at viscosity of 27 poises and refractive index 1.4895, at which point both oils have a like molecular weight of 1500.

Figure 7 shows the graph for viscosity *vs.* iodine value. Here the same facts as above noted are brought out. The final large rise in viscosity is accompanied by small decrease in iodine value. A change of 50 units (180–130) of iodine value, during which time the molecular weight increases 546 units (790 to 1336), is accompanied by an increase of only 14 poises in viscosity. Later, a decrease of 7 units (130–123) of iodine number is accompanied by an increase of 71 poises, while the molecular weight increases 314 units (1336 to 1650). It seems probable that the formation of gels means also large adsorption of ungelled molecules in such a way as to diminish the possibility of reactions of condensation or of oxidation or reduction at the double bonds. From the slope of the curve it would appear that complete saturation can never be effected in the reactions that take place during heat-bodying.

Among the curves for viscosity–acid value (Figure 8), that of the 287.8° C. (550° F.) oil is the most interesting, showing again clearly that the final large increase in viscosity, which means gel formation, is accompanied by only small increase in acid value. The temperature here has been so low that hydrolysis has proceeded slowly and only to a small extent over the long time of heating. The oil has had a chance to gel considerably with production of an acid value of less than 9. With the high-temperature oil hydrolysis has already attained its maximum value before gelation has set in to any extent.

Figure 9 shows how the oils change in color on heating. There is a large bleaching at first, with subsequent darkening. The bleaching takes place at approximately the same rate for the three oils. However, cracking reactions taking place at the sides and bottom of the kettles result in darkening, which is more evident the higher the temperature to which the oil has been heated. The color developed in the 287.8° C. (550° F.) oil on heating for 2$^1/_2$ days is not as great as that developed in the 329.6° C. (625° F.) oil in 1 day.

The relationship of refractive index to molecular weight is shown in Figure 10. The same facts which were noted in the case of the two previous oils and illustrated in Figure 2 are again presented: at first a large increase in refractive index corresponding to a small increase in molecular weight; and later the reverse, indicating molecular rearrangements rather than polymerization at first, and later polymerization or molecular packing. Attention is called to the regularity of the 287.8° C. curve. In the other two, irregularities occur which are not easily explained, but which, nevertheless, are seen in both.

The curves for refractive index–specific gravity (Figure 11) show one peculiarity. At a value around 0.956 for the specific gravity of all three oils, there are to be seen sharp changes of inflection of the curves which cannot be interpreted with certainty. Attention will be called below to the same point in connection with the curves for acid value–specific gravity.

The graph of refractive index–acid value (Figure 12) shows curves which are nearer straight lines than any of the others. The oil bodied at the lower temperature undergoes least hydrolysis while undergoing changes which determine greatest increase in index of refraction; and the oil bodied at the highest temperature undergoes greatest hydrolysis and least rearrangement resulting in increase in refractive index.

As mentioned above, there is a peculiarity in the curves for specific gravity–acid value (Figure 13). Toward the end of the processing, all the oils undergo a sudden sharp increase in specific gravity corresponding to small change in acid value. As this packing of molecules (probably gel formation) is going on, the 287.8° C. oil decreases in acid value, the 329.6° C. oil has a fixed value, and the 304.4° C. oil increases in acid value. The processes of hydrolysis and molecular condensation, involving among other factors the joining on of the acid groups, are in opposition to one another. At different temperatures they proceed at different relative rates.

Figure 14 shows the relation of refractive index to iodine value. For the 287.8° C. (550° F.) oil, corresponding to an increase from 1.4870 to 1.4905 in refractive index, the iodine value changes only from 137 to 125. The molecular-weight increase during this period is 525 units. The aggregation of molecules in gel form appears to prevent reduction of unsaturation. This plate shows throughout, the regularity with which the changes in the properties involved are taking place during the early processing at all temperatures, and throughout the entire processing period for the 287.8° C. oil.

Other pairs of properties which might have been presented have been omitted on account of exhibiting no results of special interest.

HEATS OF COMBUSTION

Long, Zimmermann, and Nevins (*3*) have already shown by determination of calorific values as well as by ultimate analysis that the hardening of linseed-oil films in dry air is partly oxidation. The few results here reported were obtained not on films, but on the raw and bodied oils in bulk. The amount of surface of oil actually exposed to the atmosphere during the cooking was necessarily small, but some oxidation was to be expected.

The first combustions were carried out in an Atwater calorimeter, with the following results:

BODYING TEMPERATURE ° C. (° F.)	TIME KETTLE WAS KEPT AT MAX. TEMP.	CALORIFIC VALUES	VISCOSITY, 25° C.
	Hours		*Poises*
Raw oil	..	9434	Less than 0.5
287.8 (550)	16	9299	85.3
304.4 (580)	4	9408	12.9
329.6 (625)	0	9326	40.4

It is noted that the greater the viscosity, the lower the calorific value; greater oxidation is accompanied by greater viscosity.

To test whether the bodied oil changed in calorific value on standing, other combustions of the same oils were made 6 months later in an Emerson bomb calorimeter:

Raw oil = 9425 cal. per gram (compare 9434)
Bodied oil = 9313 cal. per gram (compare 9299)

These latter results check well with the earlier ones, and indicate that the oils had not measurably changed on standing for this period of time.

SUMMARY

A study has been made of the changes in certain physical and chemical properties of linseed oil during the process of bodying at different temperatures. The properties studied were viscosity, color, specific gravity, molecular weight, index of refraction, and iodine value. The temperatures were 287.8°, 304.4°, and 329.6° C., and the times were 22, 9, and 9 hours, respectively. Samples were taken at regular intervals. The changes are shown to progress more regularly at lower temperatures, though slowly. At high temperature the various reactions, sometimes working in opposition to one another, change in their relative rates of speed to such an extent as to produce seeming irregularities in the experimental results. Viscosity increases from less than 0.5 to 85 poises, specific gravity from 0.925 to 0.967, molecular weight from 790 to 1600, index of refraction from 1.4800 to 1.491, and acid value from 0.445 to 14; iodine value decreases from 179.3 to 123, and color first decreases from 6 to 1, then increases to 8.5. The rates of change, as well as the extent, vary with the temperature to which the oil has been raised and the time at which it is held at this maximum temperature. Other factors also enter in. The above changes were studied in connection with time and temperature and in connection with each other. One fact that stands out is the influence of the gelation process on the reactions of the system. Not only is there a large increase in viscosity, but the gel adsorbs the ungelled molecules and seems to inhibit their reactions. Further study of the matter of gel formation and adsorption is in progress.

The relations of index of refraction to molecular weight indicate that, regardless of the temperature at which the oil is bodied, reactions of rearrangement of molecules take place before actual polymerization begins in earnest.

Some work is reported on heats of combustion, showing that the bodying process, which is partly an oxidation reaction, causes a diminution in the calorific value of the oil.

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RECEIVED September 10, 1931. Presented before the Division of Paint and Varnish Chemistry at the 82nd Meeting of the American Chemical Society, Buffalo, N. Y., August 31 to September 4, 1931. This paper is a portion of a thesis presented to the Polytechnic Institute of Brooklyn in partial fulfilment of the requirements for the degree of master of science in chemistry by J Mattiello, who is now connected with the Hilo Varnish Co., Brooklyn, N. Y

Resistance of Shellac Films to Air of High Humidity

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THE RESULTS which are obtained upon testing films are often materially influenced by factors entering into their preparation. Unless these factors are known and carefully controlled, films from the same varnish will give widely varying results.

A simple and inexpensive method for the preparation of uniform shellac films is described. This method gives films which can be easily duplicated, as judged both by weights and general behavior. A preliminary study of general factors affecting the structure and properties of films is discussed. This gives for the first time a means of controlling the method of preparation of films and of legitimate appraisal of results.

As a result of these studies it has been possible to develop bleached shellac varnishes possessing increased water resistance. It has been found that the use of 10 per cent tricresyl phosphate will impart such properties.

THE value of a protective coating depends to no small degree upon such mechanical properties as its elasticity and flexibility. So well known is the use of plasticizers in nitrocellulose varnishes that little need be said concerning their value except to recall that the success of these coatings developed with the discovery of softening agents. On the other hand, spirit varnishes, (especially shellac) possess in themselves most of the mechanical properties demanded of films, so that seldom, if ever, is anything added to them. It will be shown in this paper, however, that beneficial effects can be obtained by adding substances such as tricresyl phosphate to these latter compositions.

Factors Influencing Structure of Films

Before the effect of adding such a substance can be ascertained, it is necessary that films can be prepared which will give reliable results for comparison purposes. The behavior of films, especially those of shellac, depend to no small extent upon their method of preparation. It follows, therefore, that in such a study as this, it is absolutely essential that careful consideration be first given to this important subject.

The most important factor affecting the behavior of films is their thickness. The thickness obtained will depend to a large extent upon the ratio of solids to liquid and on the viscosity of the varnish. The viscosity in turn influences the rate of evaporation, the drying time, and the actual structure. Temperature plays a dual role affecting both viscosity and drying time.

Mechanical disturbances, atmospheric conditions, and surface tension at the edges of the test piece may alter the films. When comparing varnishes, such as those containing varying amounts of tricresyl phosphate, it is necessary that all test pieces be prepared under identical conditions; for comparison purposes this may be accomplished by preparing all the films simultaneously with recorded conditions.

Preparation of Duplicate Uniform Shellac Films

The common method of preparing films for comparison, by pouring the varnish upon a flat piece of glass inclined at a specified angle, does not give satisfactory results with shellac varnishes. Such films are wedge-shaped, and, when subjected to the action of moisture, the degree of whitening varies with the thickness. Furthermore, duplicate results cannot be obtained. It was found that ten films prepared from the same varnish by this method under the most careful conditions gave widely varying results.

On the other hand, the requirements demanded in the preparation of films can be obtained by using a very simple and inexpensive method. This consists in pouring varnishes, whose viscosities have been previously equalized in Gardner-Holt viscosity tubes, upon the center of an inverted watch glass and allowing the varnish to drain. The watch glass may be placed on any suitable support, such as a 4-ounce shellac sample bottle or similar wide-mouth bottle which will hold the watch glass in a horizontal plane. These bottles are machine-made and hence are uniform. The bottle may be placed in a Petri dish to catch the overflow varnish. A diagram of the set-up is shown in Figure 1. A hygrometer and thermometer are placed beside the apparatus to record the exact atmospheric conditions.

If several films are being prepared, it is essential that watch glasses of uniform curvature and thickness be selected. By pouring a number of varnishes at the same time, the effects of atmospheric conditions are equalized. This method of pouring films eliminates mechanical disturbances, and insures uniform flow and surface-tension effects. An ample amount of varnish should be used to provide an all-round overflow. A large piece of paper may be set around the apparatus to eliminate stray air currents.

After films have dried, which requires at least 24 hours, a centered circle which covers most of the glass is marked on the film, and the underrun and brim are carefully cut away with a razor blade up to this circle. The circumference of the circle is marked at least 1 inch from the edge of the glass. In this way the irregular thick parts of the film are removed. The shellac film remaining on the watch glass is remarkably uniform.

Shellac varnishes, approximating 5 pounds to the gallon, gave films of 0.180 gram when poured on a 4-inch watch glass. Duplicate films did not show more than 0.001 gram average difference in weight. When these were tested with moisture, they became milky simultaneously and, when air-dried, returned to transparency at an equal rate. The weight of moisture taken up by each film or lost on air-drying was equal. Furthermore, the weight of different sections of a film were equal, indicating equal thickness.

Judging the Whitening of Films

As can be seen from the tables, the degree of whitening of shellac films cannot be measured by determining the amount of water absorbed when films are exposed to moisture, as Venugopalan and Rangaswami (*4*) have assumed. It was therefore necessary to use some other measure for comparing the effects of moisture on different films. What will be termed "clearness" and "gloss" were employed for this purpose.

These terms are purely empirical, as can be seen from the methods of determining them. In determining clearness, a clear shellac film was taken for 100 per cent clearness as one point on a standard scale, and a film which had been whitened to the degree where printed matter could not be read through it, when the watch glass was placed directly over the printing, was taken as 0 per cent for the other point. An arbitrary scale for each 5 to 10 per cent was then set up by judging the maximum distance at which the test pieces could be held and the print read. All observations were made by one operator to minimize the personal factor of judgment.

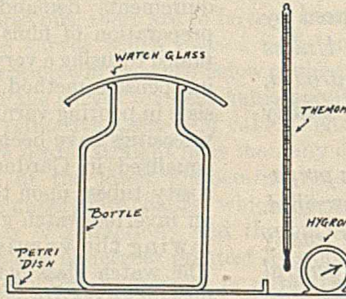

Figure 1. Device for Pouring Uniform Duplicate Shellac Films

Gloss was measured in a similar manner by noting the degree of reflection of the frame of a window when pieces were held in a position to reflect as much light as possible.

No attempt has been made in this work to reduce these values to any absolute scale, nor is any claim made for great accuracy made in their determination. They are, however, sufficiently accurate for the purpose of such a preliminary study as this. It can be seen that results are sufficiently diverse for conclusions to be clearly drawn. For these reasons it was not felt necessary to develop other methods at this time, since it is believed that more accurate measurements of degree of whitening will in no way modify the general conclusions drawn in regard to films in this paper.

General Observations on Shellac Films

Having developed a method whereby uniform and duplicate films could be obtained and a means of appraising them, it was now possible to observe quantitatively some of the factors affecting shellac films.

Thickness of Films. The effect of thickness of films of shellac in their behavior toward moisture is clearly illustrated in Table I. Samples of 3-, 4-, 5-pound cuts of the same varnish were prepared simultaneously, air-dried for 12 hours, and then further dried in an oven at 43° C. for 2.5 hours. All samples showed practically equal clearness and gloss before treatment with moisture. It can be seen that the amount of water taken up varies with the thickness of films, and that less water is absorbed on repeated contacts with moisture after air-drying. It can also be seen that the weight of moisture has no direct relationship to the degree of clarity or gloss. These observations are in accord with the conclusions of Gardner (*3*) that the absorption of moisture by shellac films is a physical phenomenon, and that the amount of moisture absorbed is related to the structure of the film and not to its composition, since in these experiments the same varnish is used throughout. The decrease which is observed in the amount of moisture that is taken up by the films on successive humidity treatments may be accounted for by making the following assumptions: Moisture is condensed in the film, causing swelling which disrupts its compact structure; this film, when dried, would then possess a structure having larger pores, which would not show the same ability of absorption and capillary condensation toward moisture.

Table I. Influence of Thickness of Film on Resistance to Moisture

Treatment	Weight of Film 3-lb. cut	4-lb.	5-lb.	Clearness 3-lb. cut	4-lb.	5-lb.	Gloss 3-lb. cut	4-lb.	5-lb.
	Gram	*Gram*	*Gram*	%	%	%	%	%	%
Dry film	0.082	0.112	0.186	90	95	85	95	98	95
After exposure to air of high humidity	0.084	0.112	0.192	90	90	80	95	95	75
After air-drying	0.081	0.112	0.180	90	90	75	95	95	95
After 2nd exposure to air of high humidity	0.081	0.109	0.178	75	75	50	80	75	60

Rate of Drying. When films are prepared in confined spaces where normal evaporation cannot take place, the slow evaporation causes the wax in a shellac film to separate. In this way permanently mottled films only are obtained. This separation of wax, although destroying the clarity of the film, does not appear to materially affect its behavior toward water.

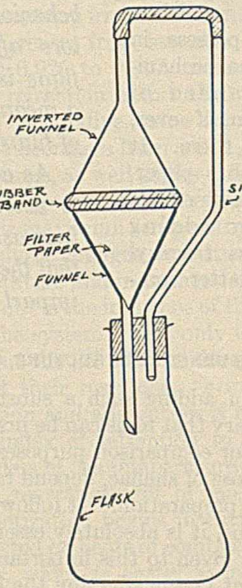

Figure 2. Filtering Device for Shellac Varnish

On the other hand, if films are subjected to moist conditions before they dry thoroughly they will become opaque more readily than films which have lost all their alcohol. This is illustrated in Table II. If "green" films are not subjected to the action of moisture for too long a period before they are air-dried, they will finally approach in resistance a state not far removed from that of the previously dried films.

Table II. Effect of Alcohol in a Film on Resistance to Moisture

Treatment	Clearness Dry film	Clearness Green film	Gloss Dry film	Gloss Green film
	%	%	%	%
After exposure to air of high humidity	95–75	75–50	75	75
Air-dried	90	95–90	80	95–75
After 2nd exposure to air of high humidity	85–75	75–60	75–60	60–40
Air-dried 2nd time	75–60	75–60	75–60	60–40

Drying in Humid Air. These observations were further confirmed by comparing films dried under humid conditions with those dried in a desiccator. As can be seen from Table III, there is little or no difference in the appearance of the two films when subjected to the different treatments, but the amount of water absorbed or lost is quite different. After the second moisture treatment and air-drying, the two films are practically identical.

TABLE III. EFFECT OF DRYING UNDER HUMID CONDITIONS

TREATMENT	WEIGHT OF FILM Dried in humidifier	WEIGHT OF FILM Dried in desiccator	CLEARNESS Dried in humidifier	CLEARNESS Dried in desiccator	GLOSS Dried in humidifier	GLOSS Dried in desiccator
	Gram	*Gram*	%	%	%	%
Untreated	0.100	0.107	95	95	95	95
After exposure to air of high humidity	0.107	0.115	95	95	95	95
Air-dry	0.098	0.102	95	95	95	95
After 2nd exposure to air of high humidity	0.114	0.120	20	15	65	50
After 2nd air-drying	0.097	0.097	70	75	80	85

It was observed that repeated treatments with moisture with intermittent drying had a far greater deteriorating effect on shellac films than continued contact with moisture. The method of repeated treatments used in this study may be considered as one of subjecting the films to the most severe conditions. The deterioration which eventually takes place may be looked upon as a result of fatigue from continual bending of the fine particles of the film by the swelling and contraction caused by the moisture. Conditions as severe as these are not usually encountered in the use of shellac varnishes.

Drying films in an air oven at 105° C. destroys the surface of the films, but films so treated are unquestionably free from all traces of alcohol. Such films were shown to absorb moisture to the same degree as the desiccator-dried films cited above. Water was taken up more slowly, however.

EFFECT OF WAX. It is well known that the condition of wax in a shellac varnish affects the drying properties of its films. For example, when a varnish is stored near a radiator, some of the wax dissolves in the alcohol at the elevated temperature. On cooling, this wax separates as a gel and yields a varnish which will not dry.

In order to study the effect of the presence of wax of normal condition in a shellac varnish, 5-pound cuts of shellac were filtered in an apparatus such as is shown in Figure 2. This consists simply of an inverted funnel joined to another in a vertical position by means of a rubber band. The vertical funnel is set in a flask and a side arm is connected to the stem of the inverted funnel by means of a rubber tube. In this manner heavy cuts of shellac may be filtered without loss of solvent during the long period necessary for such a filtration.

It can be clearly seen from Table IV that heavier films are obtained with the original varnishes, resulting from the wax imparting a greater viscosity to these solutions. Since the object of this experiment was to compare varnishes as they are commonly used, the viscosities were not equalized as was done in later experiments. The fact that the wax-free varnishes here appear to show greater resistance to moisture may be explained on the basis that the films of the wax-free varnishes are thinner (Table I).

TABLE IV. EFFECT OF REMOVAL OF WAX FROM SHELLAC VARNISHES

TREATMENT	WEIGHT OF FILM 1	2	3	4	5	CLEARNESS 1	2	3	4	5	GLOSS 1	2	3	4	5
	Gram	*Gram*	*Gram*	*Gram*	*Gram*	%	%	%	%	%	%	%	%	%	%
Untreated air-dried	0.625	0.198	0.375	0.196	0.445	95	98	90	98	95	98	98	90	98	98
After ventilated-chamber treatment	0.609	0.186	0.369	0.192	0.432	90	95	90	95	95	98	95	95	95	95
After still-air chamber treatment	0.638	0.198	0.421	0.219	0.453	5	75	10	35	5	50	75	25	80	50
After 2nd air-drying	0.595	...	0.365	0.188	0.420	60	60	50	60	60	25	25	25	40	50

1. 5-lb. cut superfine orange shellac varnish.
2. Same filtered free of wax.
3. 5-lb. cut bone-dry bleached shellac varnish.
4. Same filtered free of wax.
5. Same as 1, treated with a little oxalic acid and centrifuged.

METHODS OF TREATING FILMS WITH MOISTURE. The method of treating films with moisture will determine the degree of whitening obtained. In these studies two methods have been employed for treating films with moisture. In both cases saturated humidity at room temperatures has been used. In the first case, films were brought in contact with moisture by simply placing them in a bell jar containing a vessel of water. This method had the disadvantage of permitting actual dew formation on the film when the room temperature is slightly lowered. In the second case, films were placed in a humidity chamber where conditions were so arranged as to prevent this dew formation. This was accomplished by means of an arrangement such as is shown in Figure 3. Here the air is saturated by bubbling through water and then through a vessel containing moist cotton to which a breathing tube is attached.

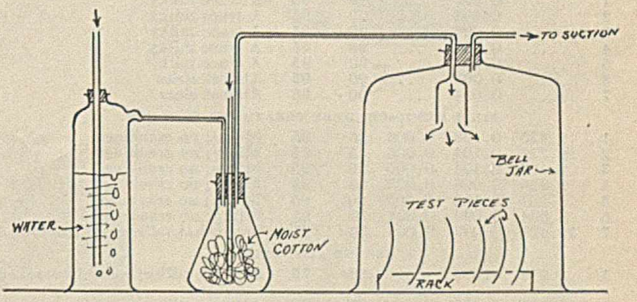

FIGURE 3. VENTILATED HUMIDITY CHAMBER

It was found that, when actual condensation took place on the shellac films, the effects were much more severe than when a ventilated humidity chamber was used. This can be seen by comparing the data given in Table IV. In these experiments the films were left in the ventilated chamber for 13 days. No great change in the various films took place. On the other hand, when they were placed in the closed bell jar in which water was placed at 28–30° C. daily to insure condensation, the films went to pieces completely in 4 days. Unless otherwise stated, films were treated by subjecting them to this latter more severe manner.

TRICRESYL PHOSPHATE IN BLEACHED SHELLAC VARNISHES. Because of its very high boiling point, tricresyl phosphate will be left in a dry shellac film. It is not unreasonable to expect that this substance might have some plasticizing effect upon these dry films of shellac from its marked behavior in this manner in nitrocellulose lacquers. If this were true, increased resistance to water would be expected, since the above studies have indicated that films deteriorate most rapidly under conditions of repeated swelling and contraction. Increased flexibility would therefore add increased life to the films. Furthermore, it is possible that liquids of this type, which absorb little or no water themselves, might fill any small pores of the films and to some extent reduce the amount of water absorbed by them. Finally, tricresyl phosphate has a refractive index of 1.56 (*2*), while bleached shellac has been shown to have a refractive index of 1.534 (*1*). Hence it would not be expected that the tricresyl phosphate held in the film would refract light to any appreciable extent, nor that films containing this liquid would have the same appearance as unplasticized films.

TABLE V. EFFECT OF ADDING UP TO 10 PER CENT TRICRESYL PHOSPHATE TO SHELLAC VARNISHES

(Films prepared from varnishes containing 45.4 grams bleached bone-dry shellac, cut in 75.7 cc. of 95% alcohol and poured on 3-inch watch glasses at 56° F. (13.3° C.) and 51% humidity. 1¹¹/₁₆-inch circles used for study.)

Film 1 contained no tricresyl phosphate	
Film 2 contained 0.045 gram tricresyl phosphate	0.1
Film 3 contained 0.227 gram tricresyl phosphate	0.5
Film 4 contained 1.454 grams tricresyl phosphate	1.0
Film 5 contained 1.908 grams tricresyl phosphate	2.0
Film 6 contained 2.270 grams tricresyl phosphate	5.0
Film 7 contained 4.540 grams tricresyl phosphate	10.0

FILM	WEIGHT Glass and film	WEIGHT Film only	WEIGHT Net change	CLEARNESS	GLOSS	APPEARANCE
	Grams	*Gram*	*Gram*	%	%	
AIR DRY FILMS						
1	....	0.097	...	90	95	A trace milky
2	....	0.098	...	90	95	A trace milky
3	....	0.096	...	90	95	A trace milky
4	....	0.093	...	90	95	A trace milky
5	....	0.098	...	90	95	A trace milky
6	....	0.095	...	90	95	Almost clear
7	....	0.094	...	90	95	Almost clear
FIRST HUMID-CHAMBER TREATMENT, 24 HOURS						
1	9.425	0.103	0.006	15	95	Milky; no cracking
2	10.712	0.104	0.006	15	95	Milky; no cracking
3	9.490	0.101	0.005	20	95	Milky; no cracking
4	8.956	0.098	0.005	20	95	Milky; no cracking
5	8.707	0.103	0.005	20	95	Milky; no cracking
6	8.994	0.099	0.004	30	95	Milky; no cracking
7	10.429	0.097	0.003	50	95	Somewhat milky; no cracking
SECOND AIR-DRYING						
1	9.418	0.096	...	80	75	Slightly milky; coarsely cracked all over
2	10.704	0.096	...	85	80	A trace milky; coarsely cracked all over
3	9.483	0.094	...	85	85	A trace milky; coarsely cracked all over, but less than 1
4	8.950	0.092	...	85	85	A trace milky; coarsely cracked all over
5	8.700	0.096	...	90	90	A trace milky; a few cracks only
6	8.988	0.093	...	95	98	Clear; no cracking
7	10.425	0.093	...	95	98	Clear; no cracking
SECOND HUMID-AIR CHAMBER						
1	9.419	0.097	...	50	75	Milky; cracked coarsely, densely
2	10.707	0.099	...	60	75	Milky; cracked coarsely, densely
3	9.486	0.097	...	60	75	Milky; cracked coarsely, densley
4	8.952	0.094	...	65	75	Milky; cracked coarsely, densely
5	8.696	0.092	...	75	75	Milky; cracked coarsely, densely
6	Broke	...	...	80	90	Milky, few cracks
7	10.427	0.095	...	85	90	Milky, no cracks
THIRD AIR-DRYING						
1	9.414	0.092	...	60	75	Slightly milky; cracked densely, coarsely
2	10.702	0.094	...	75	75	Slightly milky; cracked densely, coarsely
3	9.481	0.092	...	75	75	Slightly milky; cracked coarsely and profusely finely
4	8.946	0.088	...	75	75	Slightly milky; cracked coarsely and profusely finely
5	8.691	0.087	...	75	75	Slightly milky; cracked coarsely and profusely finely
6	Broke	...	...	85	90	Nearly clear; 1–2 coarse cracks; profusely very finely cracked
7	10.422	0.090	...	90	90	Clear; no cracks

Table V gives results for seven varnishes prepared from the same sample of bone-dry bleached shellac containing varying percentages of tricresyl phosphate from 0.1 to 10. It can be seen that the addition of this plasticizer gives very marked increased resistance to treatment with moisture, especially when added to the extent of 10 per cent. The addition of this reagent further enhances the general appearance of the films when they are dried under the slightly humid conditions with which these films were prepared. The plasticizer retarded absorption of water during the first humid-chamber treatment. The film containing 10 per cent tricresyl phosphate absorbed only half the amount of water as compared with that of the unplasticized film. On air-drying they returned to within 1–2 mg. of their original weight. On second treatment in the humid chamber, less water was absorbed than in the first. This time they gained equally in weight and were within 1 mg. of the original weight. However, the clearness fell to 50–85 per cent, and the gloss to 79–90 per cent, the low figures corresponding to films containing little or no plasticizer. The third air-drying caused films to lose 4–5 mg. in weight. Films containing less than 5 per cent tricresyl phosphate lost their clearness and gloss, whereas the 5 and 10 per cent plasticized films were little affected or not at all. The plasticized films became milky more slowly, and those containing large amount of tricresyl phosphate had a far less tendency to crack on repeated moisture treatment. The beneficial effects of tricresyl phosphate are even more strikingly illustrated in Figure 4 when pictures of these films are compared.

Table VI shows that there is little to be gained by adding greater amounts of tricresyl phosphate than 10 per cent, except possibly in a few cases where films are to be subjected to very extreme conditions. Films containing as much as 25 per cent show little difference in behavior from those containing 10 to 15 per cent.

TABLE VI. EFFECT OF ADDING GREATER THAN 10 PER CENT TRICRESYL PHOSPHATE TO SHELLAC VARNISHES

(Films prepared from varnish containing 22.7 grams of bleached refined shellac dissolved in the following:

FILM	WEIGHT	ALCOHOL	TRICRESYL PHOSPHATE	
	Grams	%	*Grams*	%
1	30.88	95	None	
2	29.74	95	1.14	5
3	28.61	95	2.27	10
4	27.47	95	3.41	15
5	26.34	95	4.54	20
6	25.20	95	5.68	25

These were poured on 4-inch watch glasses and 3-inch circle of film used for test.

FILM	WEIGHT Glass and air-dry film	Film only	CLEARNESS	GLOSS	APPEARANCE
	Grams	*Gram*	%	%	
AIR-DRY FILMS					
1	24.136	0.209	98	98	Clear
2	18.712	0.254	98	98	Clear
3	21.657	0.285	98	98	Clear
4	18.343	0.277	98	98	Clear
5	22.154	0.318	98	98	Clear
6	20.011	0.340	98	98	Clear
VENTILATED HUMID-CHAMBER TREATMENT, 13 DAYS					
1	24.131	0.204	90	90	Somewhat milky; profusely finely (hair) cracked
2	18.709	0.251	95	98	Clear; no cracks
3	21.654	0.282	98	98	Clear; no cracks
4	18.341	0.275	98	98	Clear; no cracks
5	22.152	0.316	98	98	Clear; no cracks
6	20.008	0.337	98	98	Clear; no cracks
STILL-AIR HUMID-CHAMBER TREATMENT 4 DAYS, WITH DEW FORMATION					
1	24.162	0.235	10	50 (25)	Opaque; cracked profusely, peeled at cracks
2	18.742	0.284	10	60	Opaque; no cracks, no peeling
3	21.683	0.311	10	70	Opaque; no cracks, no peeling
4	18.370	0.304	15	70	Opaque; no cracks, no peeling
5	22.189	0.353	15	70	Opaque; no cracks, no peeling
6	20.039	0.368	25	75	Opaque; no cracks, no peeling
SECOND AIR-DRYING AFTER 30 HOURS					
1	....	...	50	0	Milky; most of coating has cracked and peeled off glass, part still adhering has pearly sheen but no gloss; what is left on glass is cracked profusely
2	18.703	0.245	60	60	Somewhat milky; profusely cracked; no peeling
3	21.648	0.276	85	90	A trace milky; sparingly coarsely grooved; no peeling
4	18.338	0.272	95	95	Faint trace of separation; no cracking; no peeling
5	22.149	0.313	95	95	Clear; no cracking; no peeling
6	20.008	0.337	95	95	Clear; no cracking; no peeling
AIR-DRYING AFTER 11 DAYS					
1	....	...	..	..	Film mostly peeled off glass; appearance of remaining part same as on 3/31/31
2	18.702	0.244	60	60	Milky; profusely cracked; no peeling
3	21.648	0.276	85	90	Slightly milky; sparingly coarsely cracked; no peeling
4	18.338	0.272	95	95	Faint trace of separation in radial design resembling fingerprint; no cracks
5	22.149	0.313	95	95	Same
6	20.008	0.337	95	95	Clear; clear etching on surface; no cracking

Table VII summarizes a series of results using tricresyl phosphate in a number of bleached shellac varnishes selected from three sets of experiments.

The films of the bleached bone-dry shellac were air-dried for 4 days, and then placed in a humid chamber containing still saturated air for 24 hours. They were then allowed to air-dry at room temperature for 6 days and given a second humid treatment for 20.5 hours. The final observations given in the table were made after air-drying for 35 days.

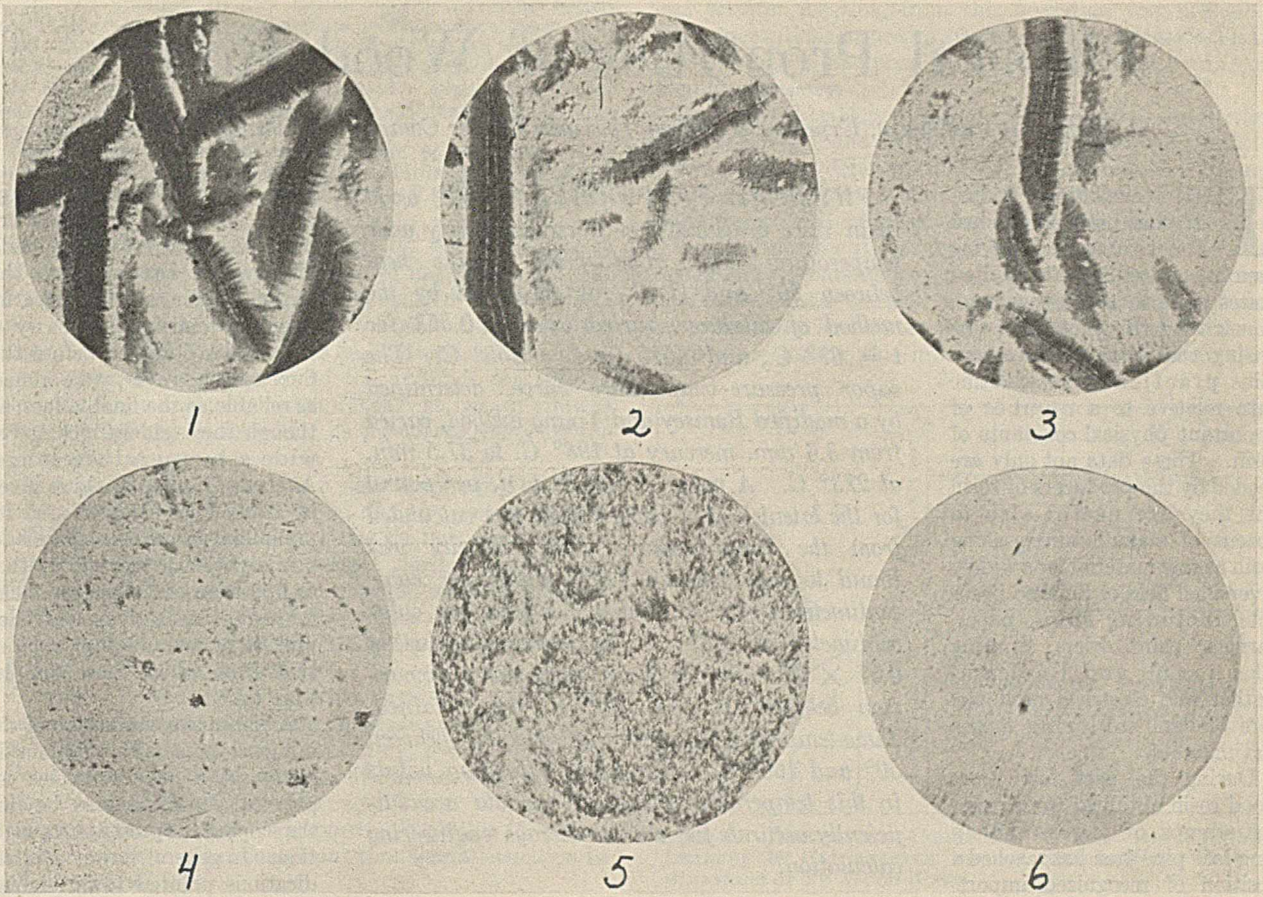

Figure 4. Effect of Moisture on Films (× 20)

1. Bone-dry bleached shellac 0% tricresyl phosphate
2. Bone-dry bleached shellac 1.0% tricresyl phosphate
3. Bone-dry bleached shellac 2.0% tricresyl phosphate
4. Bone-dry bleached shellac 10.0% tricresyl phosphate
5. Refined bleached shellac 0% tricresyl phosphate
6. Refined bleached shellac 10.0% tricresyl phosphate

Table VII. Effect of Tricresyl Phosphate on Bleached-Shellac Varnishes

Material	Amount of Tricresyl-phosphate	Clearness	Gloss	Appearance
	%	%	%	
Bleached bone-dry shellac	None	60	75	Slightly milky; cracked coarsely
	10	90	90	Clear; no cracks
Bleached refined (wax-free) shellac	None	25	0	Deteriorated; cracked up to fine particles; peeled off 95%
	25	95	95	Clear; no cracking
Bone-dry	None	50.25	25.5	Milky to white; coarsely sparingly cracked
	10	90	75	A trace milky; no cracks
A. & R. free	None	60	50	Somewhat milky; coarsely sparingly and finely profusely cracked
	10	95	90	A trace milky; no cracks
Refined	None	80	75	Somewhat milky; coarsely and finely cracked
	10	95	95	A few coarse cracking lines
French refined	None	98	98	Clear; no cracks
	10	98	95	Clear; no cracks

The bleached refined (wax-free) shellac films were air-dried for 8 days and then treated in the ventilated humid chamber (Figure 3) for 11 days. They were then air-dried for 3 days and subjected to moisture in a still-air chamber to which water at 28–30° C. was frequently added to produce a series of dew formations for 4 days. The given observations were made after air-drying for 11 days.

The bone-dry, the A. and R. free, the refined, and the French refined shellac films were air-dried for 5 days and placed in a still-air humid chamber at room temperature overnight. After air-drying for 14 days, they were subjected to a second humid treatment with frequent dew formations for 18 hours. Observations are given after air-drying for 4 days.

In all cases the plasticizer increased the water resistance. It would appear from the third part of this table that refined shellacs are more resistant to moisture than the grades containing wax. This, however, as previously pointed out, is due to the thicker films obtained with the wax containing varnishes.

It is recommended that the tricresyl phosphate be added only to fresh cutting of bleached shellacs, and that the mixtures be applied without delay, as long standing or storage of these mixtures may bring about a condition of slow drying.

ACKNOWLEDGMENT

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Physical Properties of Wood Rosin

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PHYSICAL PROPERTIES of FF wood rosin were measured over a comparatively wide temperature range. The mean specific heat between 20° and t° C., as measured by the method of mixtures, varied between 0.453 for t = 67° C., and 0.525 for t = 245° C. The vapor pressure–temperature curve, determined by a modified Ramsey and Young method, varied from 3.6 mm. mercury at 198° C. to 37.5 mm. at 273° C. A value of 105 B. t. u. per pound for the latent heat of vaporization was calculated from the vapor-pressure data. Density was found to vary between 1.089 grams per cubic centimeter at 20° C. and 0.933 gram per cubic centimeter at 238° C. A calculated value of 6.37 × 10⁻⁴ for the mean coefficient of expansion between 0° and 100° C. was obtained. Time-temperature curves investigated between 50° and 160° C. indicated no transition points in this temperature range. The data are sufficiently accurate for use in average engineering calculation.

The Naval Stores industry has been established for centuries, having been introduced into the United States more than 300 years ago. Considering this fact, it is surprising that the literature contains practically no scientific data relative to a number of important physical constants of rosin. These data not only are needed by the producers of rosin but they are useful also to dozens of manufacturers using rosin as raw material for a widely diversified field of finished products, including soap, paper, varnish, paint driers, printing inks, roofing and linoleum, leather and electrical products, core binders, soldering fluxes, and matches.

During the past few years wood rosin obtained from resinous stumps of the southern long-leaf pine tree has reached a position of recognized importance in the industry. This investigation was undertaken to study wood rosin and to measure several of its physical constants.

The determination of the physical constants of rosin presented unusual difficulties because of its low thermal conductivity and the resulting slow approach to temperature equilibrium. For this reason, it was necessary in most cases to use modifications of standard methods for the determinations. The wide change in viscosity over the temperature range studied was also troublesome. In every case, however, an attempt was made to measure the constants with the greatest possible accuracy that was significant and consistent with the method of sampling.

SAMPLES

The problem of sampling for work of this kind usually involves a careful purification of materials used. For this investigation, however, one must realize that rosin is not a pure compound but consists of a number of components of which abietic acid is the most important, usually comprising 80 per cent or more of the rosin. Rosin is graded according to certain properties, such as color, "melting point," method of manufacture, etc.; thus, the physical properties of a given grade will vary between small limits. It is then impossible to purify rosin without changing its grade.

However, most wood rosin is produced by a carefully controlled steam distillation and solvent process which gives a uniform product. The sample used for this work was taken from regular operation and can be considered representative of the ordinary run of rosin. It may be best defined by the chemical and physical analysis given in Table I, which were determined in the usual manner. FF wood rosin was selected because, until recently, it has constituted the larger portion of all wood rosin produced.

During the development of suitable methods for obtaining these data for the various properties, several preliminary determinations were made. The results recorded in this paper, in general, are those for only the final run. Many of the results obtained before this final run, however, were almost as reliable as the final values, although they seldom included as wide a temperature range. Analyses, similar to those given in Table I, of samples used for preliminary work were not made, but experience has shown that composition variations are small for rosins from a given controlled process of manufacture, such as that from which these samples were taken.

A rigorous examination of the influence of small variations in composition on the values for physical constants was beyond the scope of the present investigation. In general, however, all indications pointed toward small effects except in the case of vapor-pressure data where results varied appreciably with the sample. For example, the results for the mean specific heat given in Table II include those for three different samples, and the percentage deviation given in the last column, which includes deviations due to composition as well as experimental variation, shows satisfactory agreement between samples.

Table I. Analysis of FF Wood Rosin

Acid number	154
Saponification number	166
Unsaponifiable matter, %	9.3
Gasoline-insoluble matter, %	5.8
Specific rotation, degrees	+9.6
Color (Lovibond scale)	Amber 80, red 95
"Melting-point" drop method, ° C.	79.5

Both preliminary and final results were examined and considered in estimating the accuracy of the reported results. In general, all of the results, for which a definite reason could not be assigned to show them to be unreliable, fall within the stated degree of accuracy mentioned under the respective discussion of results. For work of this nature, where a high degree of accuracy is impossible, reporting results in the manner outlined should not detract from their value or utility and is justified upon the basis of space saved for their recording.

SPECIFIC HEAT

METHOD. The method of mixtures was used for specific-heat determinations. The experimental procedure was essentially as follows:

A known weight of rosin was placed in a copper sample bottle of about 40 cc. capacity, shown in *A*, Figure 1. This was suspended centrally by a thread or fine wire in the vapor heater, *I*, and heated until temperature equilibrium was reached as indicated by thermometer *E*. The temperature of sample and calorimeter were read, and the sample quickly dropped into the calorimeter, *C*, containing a suitable liquid which was uniformly stirred. In addition to the initial calorimeter temperature, read on thermometer *D*, temperature readings were taken 1, 3, and 5 minutes after the introduction of the heated sample, and then at regular intervals of 5 minutes each for 2 or 3 readings after the maximum reading was obtained. Water-jacket temperatures, adjusted to approximately room temperature, were measured every 5 minutes.

Temperatures of the calorimeter, rosin sample, and water jacket were read by means of special calibrated thermometers with an accuracy of ±0.01°, ±0.05°, and ±0.1° C., respectively.

Previous determinations were made for the heat capacity of the sample bottle and for each part of the calorimeter. It was also necessary to determine the specific heat of Nujol which was substituted for water in the calorimeter when the temperature of the heated sample became sufficiently high to cause appreciable vaporization of the water at the time of introducing the sample. A value of 0.447 calories per gram at room temperature was found for its thermal capacity by the method of mixtures.

The copper sample bottle had a tight screw cap which prevented access of calorimetric liquid during a determination. A sufficient air pocket was left in filling the bottle with sample to permit expansion of the sample during heating. At higher temperatures where the expansion was considerable, the top was not tightened until the sample was almost heated which permitted most of the air above the sample to escape and eliminated excessive pressures.

THERMAL LOSSES. The greatest errors in calorimetry usually arise in temperature measurements and in the estimation of thermal leakage. Unfortunately, owing to the low thermal conductivity of the sample, 45 minutes to 1 hour were usually required for temperature equilibrium in the calorimeter after the sample was dropped. With this long time interval it was even more important that special attention be given to thermal losses.

For the purpose of making the radiation corrections as small and as constant as possible, a water jacket, *J*, of about 1500 cc. capacity was used for shielding the calorimeter from outside temperature changes. The jacket was nickel-plated and polished on the inside, and was heavily lagged with felt on the outside. The inner copper vessel, *F*, was nickel-plated and polished on the outside, and rested on a cross-shaped wooden insulating support, *G*.

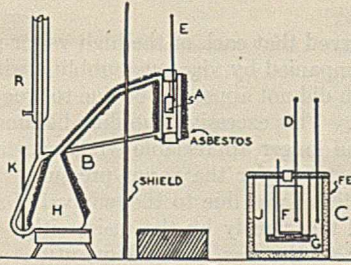

FIGURE 1. SCHEMATIC DIAGRAM OF APPARATUS FOR SPECIFIC-HEAT DETERMINATIONS OF FF WOOD ROSIN

Before each determination the calorimeter liquid was cooled to a temperature below that of the jacket water by more than one-half the temperature rise resulting from the introduction of the heated sample. By this method the calorimeter received heat by radiation during the first part of the time between the introduction of the sample and the final equilibrium temperature, and during the second part it lost heat. It was desirable to cool the calorimeter water by more than one-half the rise, since its temperature rise was most rapid immediately following the dropping of the sample. The calorimeter was brought close to the heater only for a few seconds required for introducing the heated sample, and the heat transfer resulting from this operation was negligible. These precautions insured a small and uniform thermal leakage for which it was possible to make corrections with considerable accuracy.

The thermal leakage resulting from radiation, conduction, evaporation of liquid in the calorimeter, thermal effects of stirring, etc., was determined as a single correction; no attempt was made to separate it into any of its components. Under conditions which duplicated those used during a determination of specific heat, the rise or drop in temperature of the calorimeter and its contents for a 5-minute time interval was carefully measured for various temperature differences between the calorimeter and water jacket. Plotting the change in temperature during this interval against the difference between the calorimeter and jacket temperatures, straight lines (Figure 2) were obtained for the thermal-leakage correction curves for both water and Nujol in the calorimeter.

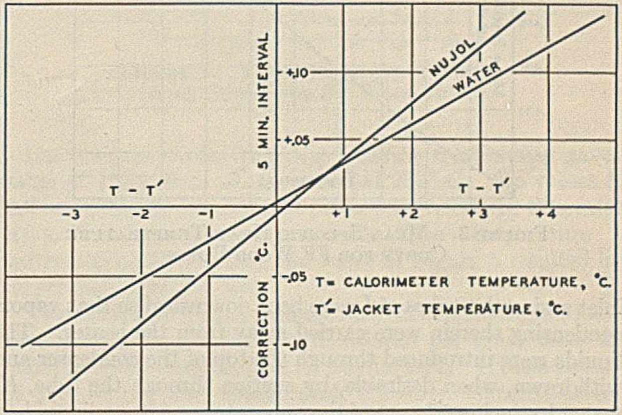

FIGURE 2. TEMPERATURE-CORRECTION CURVES FOR THERMAL LEAKAGE OF CALORIMETER DURING SPECIFIC-HEAT DETERMINATIONS OF FF WOOD ROSIN

If the thermal leakage were due entirely to radiation and conduction, Figure 2 would show straight lines passing through the origin with slopes corresponding to the relative specific heats of water and Nujol, corrected for the heat capacity of the calorimeter and contents. However, when the temperatures of the calorimeter and jacket are the same, there is a small negative temperature correction for Nujol in the calorimeter, probably due to the heat of stirring. For water under like conditions, the cooling, resulting from vaporization, more than balances the thermal effect of stirring with the net effect of a positive correction. Changes in the relative humidity in the laboratory did not produce appreciable errors in this correction.

The thermal leakage of the calorimeter during a run was found by use of these curves drawn to large scale. For each 5-minute interval during a determination, the temperature of the calorimeter was corrected by an amount corresponding to the average temperature difference between calorimeter and jacket for that interval, as shown by Figure 2.

The rate of temperature change in the calorimeter was rapid immediately following the introduction of the sample. In order to obtain a better average for the temperature difference and consequently a more accurate correction, the first 5-minute interval was subdivided into three intervals. Temperatures were taken 1, 3, and 5 minutes after the introduction of the sample, and corrections, properly proportioned to the values given by the curves, were applied to each interval separately.

VAPOR HEATER. The vapor heater, *B* (Figure 1), was constructed entirely of Pyrex glass. A liter Erlenmeyer flask, *H*, served as a boiler for a suitable liquid. The vapors passed upward and circulated between the two walls of the heater proper, *I*, and ghen passed out the bottom through a tube connecting with a reflux condenser, *R*, where they were condensed and returned to the bottom of the boiler. The upper part of the boiler, the tube leading to the heater, and the heater itself were heavily lagged with asbestos cord to reduce condensation to a minimum along this path. Both inlet and outlet tubes of *I* were bent downward so that vapors condensing therein were carried away from the heater. The liquids were introduced through the top of the condenser and withdrawn, when desirable, by suction through the tube, *K*, sealed to the lowest part of the apparatus. After a liquid had been withdrawn, air was passed through the apparatus for a few moments to remove final traces of vapor. A small quantity of the new liquid could be added for washing purposes and withdrawn if necessary. The top of the tube was then sealed off in a flame, or capped by other suitable means.

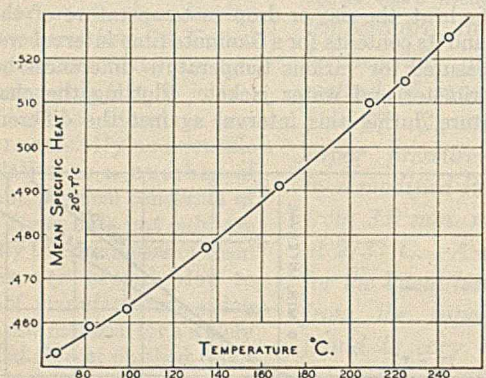

FIGURE 3. MEAN SPECIFIC HEAT–TEMPERATURE CURVE FOR FF WOOD ROSIN

Excellent circulation was obtained in the heater, and a uniform temperature could be maintained for long periods of time with little attention. With a proper selection of organic liquids, any desired temperature was obtained. Such an arrangement proved more satisfactory than an electrical tube furnace used during preliminary work.

DATA AND DISCUSSION OF RESULTS. The values for specific heat were calculated in the usual manner, and a summary of these data is given in Table II.

TABLE II. SPECIFIC-HEAT DATA FOR FF WOOD ROSIN

No. of Determinations	Temp. Range	Av. Mean C_p	Max. Deviation from Av.
	° C.		%
5	20–67	0.453	2.1
6	20–82	0.459	1.1
6	20–99	0.463	0.6
5	20–135	0.477	0.8
6	20–168	0.491	0.5
4	20–209	0.510	0.5
3	20–225	0.515	1.0
4	20–245	0.525	1.5

The recorded values are averages of three to six individual determinations and include three different samples. The maximum percentage deviation of the individual values from the average specific heat is tabulated in the last column.

The mean specific heats when plotted against temperatures give a smooth curve which closely approaches a straight line, as shown in Figure 3. It is believed that this curve is in error by not more than 1 or 2 per cent.

VAPOR PRESSURE

The method used for vapor-pressure determinations was the one developed and described by Pickett (*2*). It consisted essentially of placing the vapor-pressure tube containing the rosin sample in a special vapor bath until the temperature of the sample became constant. Then the pressure within the tube was reduced carefully until the sample began to boil. As soon as the temperature-pressure equilibrium was reached, the temperature of the liquid sample in equilibrium with its vapor was measured by a platinum resistance thermometer and the pressure of the system read on a closed-end mercury manometer sealed directly to the vapor-pressure tube. The substances used for the vapor bath for temperature control were aniline, toluidine, xylidine, diethylene glycol, glycerol, and various mixtures of these substances.

DATA AND DISCUSSION. Table III gives the data obtained from one representative run; it is noted that, for a series of observations at approximately the same temperature, each pressure reading has a lower value than the preceding ones until a constant value is reached. In addition, the drop in vapor pressure for a given series is greatest at the lowest temperatures.

TABLE III. VAPOR PRESSURE–TEMPERATURE RELATIONSHIPS FOR FF WOOD ROSIN

Temp.	Vaper Pressure	Temp.	Vapor Pressure
° C.	Mm. Hg[a]	° C.	Mm. Hg[a]
198.2	299.3	236.6	67.0
196.6	89.0	236.9	22.0
197.5	39.0	237.2	13.4
197.5	23.0	237.5	12.5
198.3	10.5	237.5[b]	12.5
198.4	5.3	250.9	24.0
198.2	4.2	251.0	19.0
198.3	4.0	251.5	19.4
198.2	3.8	251.5[b]	19.4
198.2	3.6	264.2	33.5
198.2	3.6	263.9	27.5
198.2[b]	3.6	263.9	27.5
212.5	31.5	272.7	42.0
212.5	10.9	272.7	40.3
212.5	7.8	272.7	37.5
212.3	5.6	272.7	37.5
212.2	5.4	272.7	37.5
212.1	5.4	272.7[b]	37.5
212.2[b]	5.4		

[a] At 0° C.

[b] Values used to plot vapor pressure–temperature curve.

It was observed that each of the high vapor-pressure readings was accompanied by vigorous bubbling with a tendency to foam, which did not appear to be due to true boiling of the entire sample. This excessive bubbling became less and less until it was no longer appreciable when constant successive readings were taken for the vapor pressure. It is thought that this condition was due to the removal of small traces of moisture held tenaciously by the rosin, either chemically or physically, or to the loss of small quantities of pine oil or other volatile material. The pressure measured when these substances were being removed was not the true vapor pressure of rosin itself, while pressures which remained constant for successive evacuations at a given temperature no doubt represented nearly the true vapor pressures. Figure 4 is drawn from these lower constant values.

Appreciable decomposition was noted at temperatures above 280° C. which made readings unreliable. Readings taken at 180° C. indicated that the vapor pressure was less than 1 mm. at that temperature. The difficulties associated with this problem made accurate determinations practically impossible, and the results may be in error by as much as 10 per cent.

EMPIRICAL METHODS. A number of empirical methods have been evolved to extrapolate vapor-pressure data, and, while such methods cannot be expected to be universally true, they are often useful in extending vapor-pressure curves with a fair degree of accuracy. Owing to the apparent instability experienced with each successive increase in temperature, empirical methods are likely to be less applicable in this particular case; but, in order to satisfy a need for approximate vapor-pressure data to include a relatively small temperature range above 280° C., such a method was employed. In actual rosin distillation this condition of instability, as described, is less significant to the process as a whole than it is in a vapor-pressure determination.

Dühring's rule was selected as the method to be used. This relationship is based upon the experimentally determined fact that, if the temperatures of the substance under investigation are plotted against the temperatures of a standard substance at which the vapor pressures of both substances are equal, the experimental points fall nearly upon a straight line. This assumes that any deviations from the theoretical vapor-pressure equations found in the substances must be equal and in the same direction, if the rule is to hold. Consequently, it is desirable to use for a standard substance, a compound molecularly similar and with a boiling point as near as possible to that of the substance under consideration. Alpha terpineol was selected as the standard compound since it fulfilled these conditions better than any other substance with a known vapor-pressure curve (*3*).

Such a plot results in a straight line within experimental limits, as shown in Figure 5. The dotted portion of the line represents the extrapolated values for rosin. The temperatures at which alpha terpineol and FF wood rosin have equal vapor pressures are given in Table IV. Results are given for pressures to 760 mm. mercury (409° C.). Values for the higher pressures are probably inaccurate and were included chiefly as an aid in drawing Figure 4. The dotted portions of this vapor pressure–temperature curve, plotted from the extrapolated values, should be useful in approximating vapor-pressure data to 360° C. with an error estimated not to exceed 20 per cent.

TABLE IV. DÜHRING'S RELATIONSHIP

(Comparison of alpha terpineol–FF wood rosin)

TEMP. ALPHA TERPINEOL	VAPOR PRESSURE	TEMP. ROSIN
° *C.*	*Mm. Hg*	° *C.*
73.0	3.6	198.2
82.4	5.4	212.2
99.5	12.5	237.5
108.5	19.4	251.5
124.0	37.5	272.7
142.3	73.7	300[a]
172.0	207.2	342[a]
177.6	246.0	351[a]
208.4	597.1	395[a]
217.5	760.0	409[a]

[a] These values are taken from Dühring's lines, Figure 5.

LATENT HEAT OF VAPORIZATION

METHOD OF CALCULATION. No attempt was made to determine experimentally the latent heat of vaporization of rosin. The accurate determination of this constant would have required an unwarranted expenditure of time, considering the fact that the heat of vaporization probably could be calculated from vapor-pressure data with an accuracy sufficient for engineering purposes. The methods generally used are those based upon the Clausius-Clapeyron equation or Dühring's rule.

If the value for volume of the liquid in the well-known Clausius-Clapeyron relationship is neglected, and the perfect gas equation and a constant value for the latent heat of vaporization between T_1 and T_2 assumed, the close approximation is obtained after integration:

$$\ln \frac{p_2}{p_1} = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

where ΔH = heat of vaporization per mole.

Substituting the values from Table III, $p_1 = 19.4$, $p_2 = 12.5$, $T_1 = 525$, $T_2 = 511$, and $R = 1.99$, ΔH is found to be 16,824 calories per gram mole, or 58.4 calories per gram, which is equal to 105.1 B. t. u. per pound.

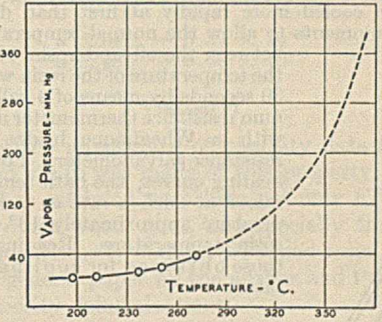

FIGURE 4. VAPOR PRESSURE–TEMPERATURE CURVE FOR FF WOOD ROSIN

Calculations made from the Dühring relationship gave a value of 103.9 B. t. u. per pound at 252° C. No values for ΔH were known for alpha terpineol; therefore, in this calculation those for water were used. The temperature *vs.* temperature plot for rosin and water in Figure 5 resulted in a surprisingly straight line.

The molecular weight used for rosin in calculating the latent heat in calories per gram from calories per gram mole was taken to be the same as that for abietic acid. If rosin consists of over 80 per cent abietic acid, the other material present must vary greatly in molecular weight from that of the acid to cause the mean molecular weight of rosin to be greatly different from that of abietic acid itself. It is further assumed that there is neither dissociation nor association of the molecules. Dissociation seems unlikely, and association at these high temperatures does not appear probable. The molecular weight used for abietic acid was 288, taken from the International Critical Tables, and is obtained from the $C_{19}H_{28}O_2$ formula.

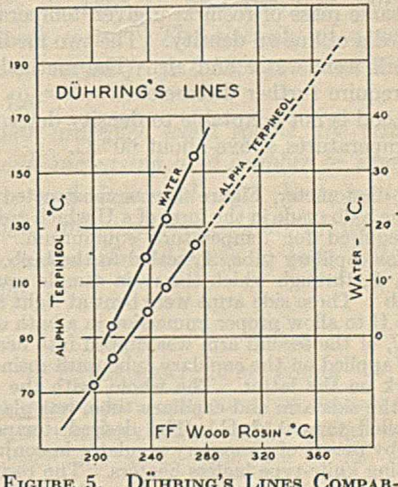

FIGURE 5. DÜHRING'S LINES COMPARING FF WOOD ROSIN WITH ALPHA TERPINEOL AND WATER

Calculations (*1*) of ΔH from data obtained later from the condenser during actual semiplant operations gave a value of 105 B. t. u. per pound. This remarkable agreement between calculated and semiplant results is probably a coincidence, since the calculations made were not considered to have this accuracy.

TRANSITION POINTS. Time-temperature curves were determined for the purpose of detecting transition points.

About 50 grams of rosin were placed in a large test tube, air-jacketed by a larger tube immersed in an oil bath heated to approximately 170° C., and the whole then allowed to cool. The oil bath cooled more rapidly at first than did the rosin. After a few moments to allow the normal temperature gradient between the oil and rosin to be reached, the temperature of the rosin was read every 30 seconds by means of a calibrated platinum resistance thermometer in conjunction with a Wheatstone bridge and a low-resistance galvanometer. For determining heating curves, the bath temperature was raised at such a rate as to keep its temperature approximately 10° C. above the rosin temperature. Readings similar to those obtained for cooling curves were taken.

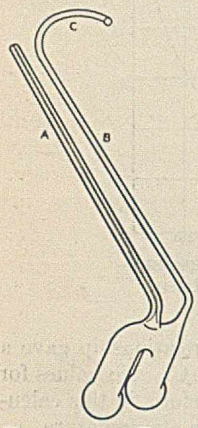

FIGURE 6. DILATOMETER FOR DENSITY DETERMINATIONS OF FF WOOD ROSIN

Typical smooth time-temperature curves were obtained in all cases within the temperature range studied (50–160° C.) which indicated the absence of transition points. Suspended transformations probably would not occur in the case of heating curves under the conditions of the experiments.

Attention is called to the fact that ordinary rosin has no true melting point. The temperature commonly referred to by the trade as the melting point is really the temperature at which the sample reaches a definite though unknown consistency. A viscosity determination is undoubtedly a better measure of this property than is the usual melting-point determination. This subject will be discussed in more detail in a subsequent paper.

DENSITY

METHODS. It was necessary to use two different methods for the density determinations of rosin over the temperature range studied. The method used at room temperature was based upon Archimedes' principle and necessitated the weighing of the same mass of rosin at a given temperature in two different media of known density. The two media employed for this work were water and air. The method is too well known to require further discussion.

This method is not adaptable to density determinations of rosin at temperatures above about 60° C.

A special dilatometer, Figure 6, was constructed from Pyrex glass with the bulb made in the form of a U which greatly reduced the time required for temperature equilibrium. In addition to the regular capillary tube, *A*, sealed to the bulb, there was a second arm, *B*, through which the rosin sample was introduced into the bulb. These side arms were bent at right angles to the plane of the U to allow proper immersion in a bath of less depth. The neck, *C*, of the second arm was dipped into heated rosin as suction was applied on the capillary tube until rosin reached the bottom mark on the latter. The whole, with the exception of the tops of the side arm and capillary tube, was placed in an oil bath controlled to ±0.1° C. The desired temperature was maintained by means of a mercury regulator in conjunction with relay-operating knife-type lagless heaters. The rosin in the top of the side tube hardened and formed a plug which prevented any rise or fall of the rosin at this point.

When the temperature of the rosin became constant, the height of the meniscus in the capillary tube above the bottom mark was measured with a millimeter scale. Then the bath temperature was increased and the process repeated. A window in the insulation and an electric light in the oil bath permitted readings of the height of the rosin in the capillary to be taken without raising the dilatometer from the bath. When the meniscus rose in the capillary to almost the level of the oil in the bath, the end of the side arm, *B*, was warmed sufficiently for rosin to be removed by suction until the meniscus in the capillary was again lowered to the bottom mark. After the original filling of the instrument and after each removal of rosin, the whole was weighed.

CALIBRATION OF DILATOMETER. The weight and volume of the dilatometer at 20° C. had been previously determined. Corrections for volume changes due to the coefficient of expansion of the Pyrex glass were made for each temperature. Both water and mercury were used to determine the volume of the bulb, which was found to have a capacity of 82.9 cc. at 20° C. The diameter of the capillary tube was found by weighing the mercury required to fill a 10-cm. length. Each millimeter length of capillary had a capacity of 0.00879 cc. at 20° C.

DATA AND DISCUSSION OF RESULTS. The density data are recorded in Table V and shown graphically in Figure 7. Below 220° C., the results satisfy the relation:

$$D = 1.089 - 0.000663\ (t^\circ - 20^\circ \text{ C.}) \qquad (1)$$

The change in density resulting from prolonged heating is shown clearly in the density-temperature curve. There is a sudden change in its slope at about 225° C. which becomes very marked with increase of a few degrees in temperature. To determine whether or not this was a reversible change, rosin which had been heated for 2 hours at 235–245° C. was cooled, and the density again determined. The results are shown by the dotted line and prove that the sudden drop in the curve at 225° C. was due to some irreversible change. Whether this change resulted from isomerization, loss of volatile matter, or molecular decomposition was not studied. Some difficulty in preventing gas bubbles being entrapped in the dilatometer at temperatures above 200° C., and especially above 225° C., was indicative of molecular decomposition. A sample heated to 200° C. or less, and then cooled, had practically the same density at any given low temperature that it had at the same temperature before being heated.

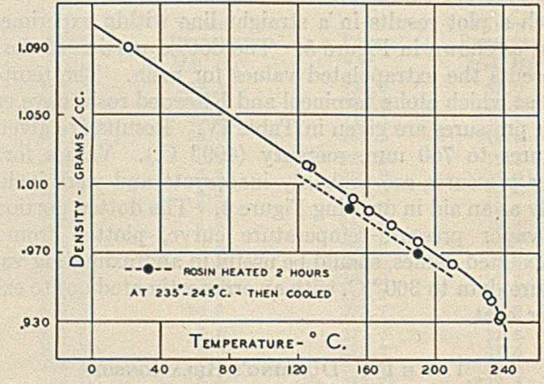

FIGURE 7. DENSITY-TEMPERATURE CURVE FOR FF WOOD ROSIN

The problem of finding a substance for a bath, which would be sufficiently transparent to permit readings being taken through it, and would be stable at these higher temperatures, presented difficulties. Several substances were tried without success. Ordinary Nujol was not suitable; but when about 50 per cent of it was distilled off at 1 cm. pressure, there remained a clear residue suitable for a transparent high-temperature oil bath.

COEFFICIENT OF CUBICAL EXPANSION

The change in volume with temperature of an isotropic substance may be expressed by the equation:

$$V_t = V_0\,(1 + \alpha t + \beta t^2 \ldots\ldots)$$

where V = volume of given mass of substance at t°

V_0 = volume of same mass at some reference temperature (usually 0° C.)
α and β = constants characteristic for each substance

Omitting the powers of t higher than t^2, and substituting $V = \frac{1}{D}$, the equation may be written:

$$\frac{D_0}{D} - 1 = \alpha t + \beta t^2$$

Substituting two sets of values for D and t calculated from Equation 1, and solving the equations simultaneously, α and β are 5.93×10^{-4} and 4.35×10^{-7}, respectively.

Table V. Density Data for FF Wood Rosin

Temp.	Density		Deviation of Calcd. from Obsvd.	Sp. Vol.
	Obsvd.	Calcd. from equation		
° C.	Grams/cc.	Grams/cc.	%	Cc./gram
20.0	1.089	1.089	0.00	0.918
126.5	1.020	1.018	0.20	0.980
127.0	1.019	1.018	0.09	0.981
152.0	1.001	1.001	0.00	0.999
162.0	0.994	0.995	0.10	1.006
174.5	0.985	0.987	0.20	1.015
190.0	0.976	0.976	0.00	1.025
210.0	0.963	0.963	0.00	1.038
230.0	0.945	...	..	1.058
231.0	0.942	...	..	1.062
237.0	0.931	...	..	1.074
238.0	0.933	...	..	1.072
190.0[a]	0.969	...	..	1.032
150.0[a]	0.995	...	..	1.005

[a] Sample heated for 2 hours at 235–245° C. and then cooled to indicated temperature.

The mean coefficient of cubical expansion, α', may be calculated by the equation:

$$\alpha' = (\alpha + \beta t)$$

The following results for FF wood rosin were calculated:

$$\alpha'_{0°-100° C.} = 6.37 \times 10^{-4}$$
$$\alpha'_{0°-200° C.} = 6.80 \times 10^{-4}$$

Viscosity

Because of the importance of viscosity data for rosins, a more detailed study was made of this property, and the investigation was extended to include not only FF wood rosin but several other wood, gum, and specially treated rosins. For this reason viscosity data for FF wood rosin are included in the more general paper by the author and Pragoff, in this issue, on viscosity determinations.

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(1) Bacon, T. S., Unpublished results obtained at Expt. Sta., Hercules Powder Co., April, 1929.
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Received April 9, 1931. Presented before the Division of Paint and Varnish Chemistry at the 81st Meeting of the American Chemical Society, Indianapolis, Ind., March 30 to April 3, 1931.

Viscosity-Temperature Relationships of Rosins

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VISCOSITY-TEMPERATURE relationships of several wood and gum rosins were studied to cover, with a few exceptions, the temperature range of 125° to 200° C. Viscosities were measured in c. g. s. units by means of a Bingham capillary-tube viscometer with an error not to exceed 1 per cent.

The viscosities of the wood rosins ranged from 2.83 poises at 125° C. and 0.068 at 200° for regular I rosin to 63.25 poises at 140° C. and 0.875 at 200° for limed rosin. The viscosities of the gum rosins ranged from 2.71 poises at 125° C. and 0.136 at 180° for grade N American rosin to 10.07 poises at 125° C. and 0.211 at 180° for grade K Greek rosin. The viscosity of a sample of abietic acid varied from 0.559 poises at 160° C. to 0.133 at 190°.

For regular untreated wood rosins, the viscosity decreased with increasing acid number or degree of purification, and increased with heat treatment, saponification, and oxidation. Rate of flow–pressure relationships showed rosin to be a truly viscous material.

It is necessary that manufacturers select carefully their raw materials in order to keep their products up to standard. Uniformity in the physical as well as the chemical properties of raw ingredients tends toward uniformity in finished products. Rosin is a raw material used very extensively in a widely diversified field of finished products, and viscosity is one of its most important physical properties. This property is one in which the users of rosins undoubtedly are very much interested in spite of the fact that the literature is barren of such data. To supply this need, viscosity-temperature relationships of various domestic wood and gum rosins, and of several foreign gum rosins were studied; and, for most of the rosins, curves were drawn to cover the temperature range of 125° to 200° C.

Experimental Procedure

Since rosin is not a pure compound but consists of a number of components, the selection of samples requires a detailed analysis of each one used. Analyses of the samples are given in Table I.

Wood-rosin samples were obtained from regular plant operation and thus may be considered to be representative of their respective grades. In the case of FF and I wood rosins measurements were made on two samples of each, obtained from the same source. Analyses of the check samples were similar although they were selected at different times. Gum-rosin samples were obtained from various sources, but should be fairly typical of their corresponding grades.

The presence of dirt in the gum-rosin samples made filtration necessary. This process consisted of melting each sample and filtering it through a glass wool and cotton plug, using suction. The operation, carried out in an oven at 125° C., was completed as rapidly as possible, since excessive heating in the open was found to drive out some of the more volatile constituents.

Table I. Analyses of Rosins

	Acid No.	Sapon. No.	Melting Point[a] ° C.	Insol. Gas %	Unsaponified %
			WOOD ROSINS		
I	161.9	171.0	77.3	0.06	7.3
Heat-treated I[c]	143	...	74	...	..
FF	153.0	163.5	78.0	5.3	9.3
Heat-treated FF[d]	138.0	...	...	...	..
Abietic acid[e]	185.5	187.0	153.0[b]	...	..
I—20[f]	144.1	151.9	84.0	0.4	8.8
195° F. limed L[g]	118.1	144.0	93.5	7.1	17.5
B	107.5	150.3	98.5	87.7	13.5
Oxidized I[h]	158.5	...	...	...	..
222° F. limed B[i]	96.0	142.7	105.5	85.0	12.5
235° F. limed L[g]	89.9	123.4	114.0	2.9	17.0
			GUM ROSINS		
American N No. 1	155.9	165.8	79.0	0.9	
American N No. 2	162.0	...	79.0	...	
Spanish N	164.8	169.4	83.5	0.2	
French WW	167.0	172.5	85.0	0.2	
Portuguese I	167.6	171.6	86.5	0.5	
American D	166.0	...	86.0	...	
Greek K	170.5	175.9	89.5	1.4	

[a] By drop method.
[b] By capillary-tube method.
[c] Prepared by heating I rosin to 300° C. for approximately 30 minutes.
[d] Prepared by heating FF rosin to 350° C. for approximately 8 minutes.
[e] Prepared from commercial abietic acid by recrystallizing three times from 80% alcohol.
[f] Prepared by adding Na_2CO_3 to drop liquor equivalent to 2% rosin by weight.
[g] Prepared by treating FF rosin with sufficient lime to raise the melting point as determined by the drop method to indicated temperature. (195° F. = 90.6° C.; 235° F. = 112.8° C.)
[h] Prepared by exposing powdered I rosin to an atmosphere of oxygen until 100 grams had picked up 8.4 grams of oxygen.
[i] Prepared by treating B rosin with sufficient lime to raise the melting point, as determined by the drop method, to 222° F. (105.6° C.).

A Bingham and Jackson viscometer (*2*) of the pipet type and made of Pyrex glass was used to determine viscosities of the rosins. This instrument is so constructed as to minimize all errors and is capable of giving absolute values for viscosity in c. g. s. units with a high degree of accuracy. The method consists essentially in measuring the time of flow for a given volume of sample (approximately 4 cc.) at a specified temperature and under a known constant pressure, through a capillary tube previously calibrated. Details of the instrument and method may be found by referring to the original paper.

For rosin samples a much more satisfactory method was found for filling the viscometer than the usual way of introducing the material by means of a small pipet. After the instrument had been thoroughly cleaned and dried, it was inverted; the open-end limb, previously warmed with a Bunsen burner, was dipped into the sample heated to 125° C. and rosin was drawn up to a predetermined mark by applying suction to the other end. Any excess rosin accidentally introduced was removed by suction through a warm, long, narrow pipet.

The viscometer was held rigidly in a thermostat by a brass frame which protected it from breakage and held it in a vertical position during all determinations. The thermostat consisted of a 5-liter Pyrex jar filled with Nujol. It was insulated with several layers of asbestos paper, through which a window was cut for observation purposes. Light was supplied by a 6.6-volt automobile headlight bulb placed behind the viscometer.

The thermostat was heated by means of lagless knife-type resistance heaters, operated intermittently by a relay and mercury regulator. A turbine stirrer provided adequate agitation. The temperature was controlled to ±0.3° C. of that desired. Because of the relatively low thermal conductivity of rosin, samples usually were placed in the bath for 20 minutes before any readings were taken, to insure uniform temperature. The only exceptions were made at the higher temperatures where there was evidence of decomposition of the sample.

Pressure was supplied from a tank filled to the desired pressure directly from the compressed-air line and was measured by means of an open-end mercury manometer. The tank was of sufficient size to prevent perceptible drop in pressure on withdrawal of small quantities of air required during a determination. Manometer readings were corrected for temperature variations.

An arrangement of vacuum-base stopcocks, sealed together, replaced the usual valve connections and proved convenient for alternately connecting the viscometer limbs to pressure and to atmosphere. At higher pressures it became necessary to modify the stopcocks by sealing to the handles of the cock, short glass tubes with hooks drawn out at each end. The cocks could then be held in place by rubber bands stretched over the hooks and around the side arms.

Time measurements, accurate within 0.2 second, were made with a calibrated stop watch.

Calibration and Calculations

The viscosities were calculated by the formula:

$$\eta = Cpt - \frac{C'\rho}{t}$$

where η = viscosity of substance, poises
C and C' = constants of individual instrument
t = time, seconds
p = pressure, grams per sq. cm.
ρ = density of sample, grams per cc.

The second term of the right-hand member of this equation is the kinetic-energy correction, which is kept small by keeping t comparatively large. For this reason C' and ρ need not be known with great accuracy, and values taken from the density-temperature curves of FF rosin (*4*) could be used for all samples in these calculations.

The value of the constant, C', was calculated from the dimensions of the instrument as outlined by Bingham (*1*). The value of the constant, C, was obtained by filling the viscometer with freshly distilled dust-free water and determining the time of flow at 20° C. The value used for the viscosity of water at 20° C. was 1.005 centipoises. Table II lists the constants of the instruments used.

Table II. Constants of Viscometers

Viscometer	Capillary Length Mm.	Radius Mm.	Vol. of Bulb[a] Cc.	C	C'
1	121.0	0.170	4.08	6.5080×10^{-7}	0.01504
2	122.4	0.190	4.02	1.0273×10^{-6}	0.01487
3	120.0	0.244	4.02	2.851×10^{-6}	0.01494
4	120.0	0.335	4.00	1.0143×10^{-5}	0.01465

[a] At 20° C.

In Tables III and IV are tabulated summaries of the viscosity data obtained for wood and gum rosins, respectively. One to twelve determinations were made at each temperature for each rosin. The temperature of the samples at the time of determination, the average value for separate viscosity determinations, and the maximum percentage deviation of individual determinations from the average viscosity are recorded. The fluidity in rhes (reciprocal viscosity in poises) was calculated and is also given.

The rate of flow–pressure data are given in Table V. The data for rate of flow were calculated by dividing the volume of the bulb, given in Table II for the instrument used, by the respective time of flow tabulated in column 2. The pressure in grams per square centimeter was calculated by multiplying the height of mercury column (column 3) by the density of mercury corrected for temperature.

These values are averages of one to six determinations. In no case did the maximum deviation of an individual determination from the mean value exceed 0.5 per cent.

Table III. Viscosity Data for Wood Rosins

Treatment	Grade	Determinations	Temp. °C.	Av. η Poises	Max. Deviation from Mean %	Av. φ Rhes
Regular	I	2	125	2.83	0.18	0.354
		3	150	0.501	0.60	1.99
		2	175	0.158	0.00	6.33
		4	200	0.068	0.59	14.7
Regular (check sample)	I	2	140	0.960	0.94	1.041
		3	160	0.318	0.19	3.150
		3	180	0.138	0.07	7.230
		4	200	0.073	0.27	13.70
Heat-treated	I	2	125	3.08	0.32	0.263
		6	150	0.521	0.58	1.92
		4	175	0.170	0.68	5.89
		4	200	0.0737	0.13	13.6
Regular	FF	1	105.0	38.1	0.00	0.263
		3	120.5	6.10	0.82	0.164
		6	130.0	2.56	0.78	0.391
		4	134.8	1.75	1.14	0.571
		4	143.2	0.965	0.31	1.04
		2	151.0	0.630	0.95	1.59
		11	153.2	0.559	1.61	1.79
		3	160.1	0.392	0.25	2.55
		12	169.0	0.248	0.81	4.03
		6	173.2	0.218	0.92	4.59
		5	181.0	0.148	0.68	6.76
		5	189.9	0.109	0.92	9.17
		5	195.0	0.0912	0.22	10.96
		4	199.6	0.0819	0.24	12.21
		4	210.0	0.0610	0.50	16.64
Regular (check sample)	FF	4	120	5.951	2.0	0.168
		4	140	1.205	1.93	0.830
		4	160	0.3675	0.95	2.721
		4	180	0.1578	0.76	6.337
Heat-treated	FF	2	125	4.230	0.00	0.236
		3	150	0.724	0.41	1.380
		4	175	0.207	0.48	4.830
		4	200	0.088	1.48	11.40
Abietic acid	...	4	160	0.559	1.07	1.790
		4	175	0.249	1.20	4.016
		3	190	0.133	0.75	7.518
Na_2CO_3	I-20	4	125	7.105	0.42	0.141
		4	140	2.165	0.56	0.462
		4	160	0.650	0.62	1.536
		4	180	0.257	0.31	3.894
		3	200	0.126	0.24	7.930
Limed, 195° F. (90.6° C.)	L	4	140	6.113	0.66	0.164
		4	160	1.575	0.70	0.635
		4	180	0.554	0.72	1.805
		4	200	0.226	0.44	4.419
Oxidized	I	1	140	13.83	0.00	0.0725
		1	150	5.29	0.00	0.189
		2	175	0.980	0.41	1.02
		2	200	0.261	0.38	3.83
Regular	B	4	140	11.02	1.36	0.0902
		4	160	2.575	0.80	0.388
		4	175	1.053	0.48	0.950
		4	180	0.808	0.50	1.24
		2	200	0.338	2.07	2.96
Limed, 222° F. (105.6° C.)	B	4	140	22.09	0.95	0.0452
		6	160	4.47	0.67	0.224
		4	180	1.141	0.44	0.876
		2	200	0.477	0.00	2.10
Limed, 235° F. (112.8° C.)	L	2	140	63.25	0.76	0.0157
		4	160	11.05	1.64	0.0905
		4	180	2.505	0.48	0.399
		4	200	0.875	0.34	1.14

Discussion of Results

A fair estimation of the accuracy of viscosity data can be obtained from a consideration of the accuracy of each operation involved. Pressure measurements always exceeded 10 cm. of mercury. The maximum error in reading was not greater than 0.3 mm., which would result in an error of not more than 0.3 per cent in the calculated viscosities even at the lower pressures. The minimum time interval used was 100 seconds, measured with an error less than 0.3 seconds. Thus, the maximum error from this source was not more than 0.3 per cent. Corrections were made for the kinetic energy of the sample. Errors in this correction and those due to drainage, fluctuations in bath temperatures, slippage, etc., were small. The maximum total error in the average reported data is estimated not to exceed 1 per cent, although the tables show that a few individual determinations deviate from the mean by as much as 2 per cent. This accuracy probably falls within the variations shown by different samples classified in the same grade.

The average viscosities, when plotted against temperatures, give smooth curves, as shown in Figures 1 and 2. All of the curves are of a similar character, convergent with increasing temperature. It is interesting to observe the rapid change in the temperature coefficient of viscosity at approximately 150° C. The crossing of the curves for wood B and oxidized wood I at approximately 165° C. is the only irregularity noted. This actually may represent the true character of the respective samples, although decomposition of the oxidized sample may account for this fact. Because Figures 1 and 2 are plotted to different scales, the curve for wood I is included in Figure 2 in order to make possible a better comparison between wood and gum rosins.

The two American gum N samples gave curves which neither coincided with each other nor with the curve for a Spanish gum N sample. This illustrates the lack of uniformity in viscosity of samples of gum rosin of the same grade. Measurements on check samples of FF and I wood rosins resulted in curves incapable of separation from those of the original samples, respectively, when drawn to the scale employed in Figure 1. It should be stated, however, that the check samples were obtained from the same plant although on different days of operation.

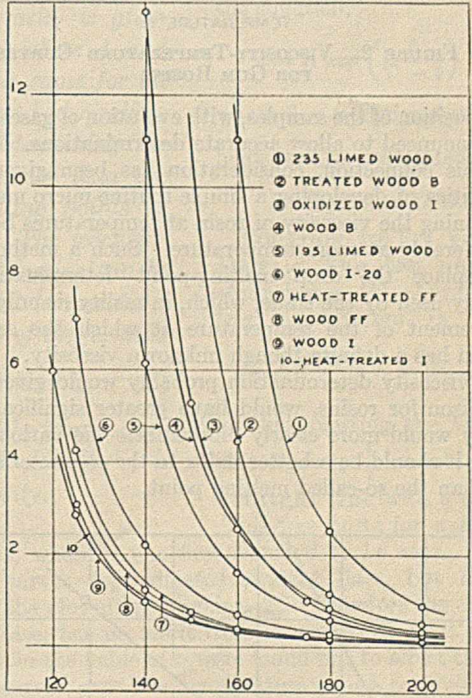

Figure 1. Viscosity-Temperature Curves for Wood Rosins

For many substances, nearly straight lines are obtained when their fluidities are plotted against respective temperatures. The fluidity-temperature curves for these rosins, however, deviate considerably from straight lines. For this reason, fluidity data for rosins offer little advantage over viscosity data for extrapolation purposes. Other methods of plotting and interpreting the data mathematically are studied in another paper (*3*).

In most cases, the viscosity was so high at temperatures below 125° C. that the time of flow was too great for its practical measurement when using the viscometer employed at higher temperatures. At temperatures above 200° C. the

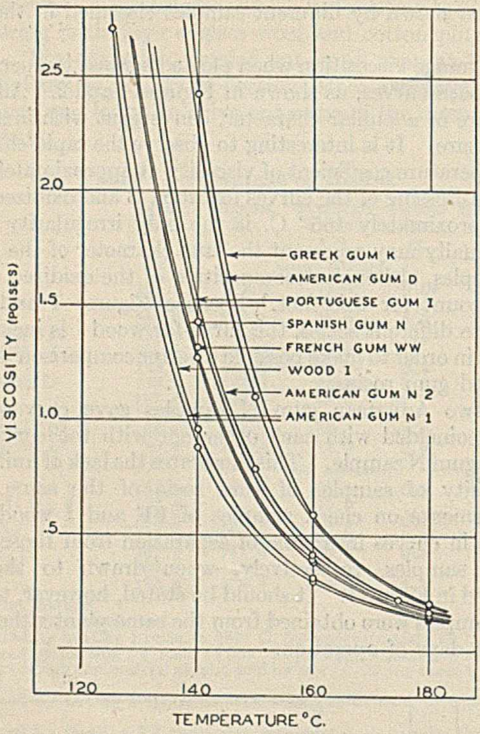

FIGURE 2. VISCOSITY-TEMPERATURE CURVES FOR GUM ROSINS

decomposition of the samples, with evolution of gases, became too pronounced to allow accurate determinations.

In this connection, consideration has been given to the possibilities of developing a simple routine micro method for determining the viscosity of rosin at temperatures below 60° C., preferably at room temperature. Such a method might well replace the drop melting-point determination now generally used by the trade, which, in reality, is only a crude measurement of the temperature at which the sample in question has a definite though unknown viscosity. It is felt that a viscosity determination probably would give a better comparison for rosins, would have greater significance, and possibly would more clearly differentiate the various rosins; that is, it should be a better index to the characteristics of a rosin than the so-called melting point.

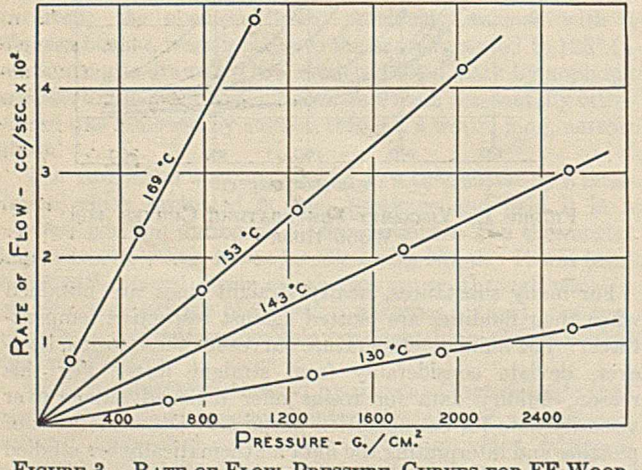

FIGURE 3. RATE OF FLOW–PRESSURE CURVES FOR FF WOOD ROSIN

The rate of flow–pressure data included in Table V and plotted in Figure 3 were obtained in order to establish whether rosin was a viscous or plastic substance. The behavior of these two types of materials differs when subjected to successive increasing pressures. For a given capillary, the rate of flow of a viscous substance is proportional to the pressure, while the rate of flow for a plastic material is proportional to the pressure in excess of a certain value. The straight flow-pressure lines for rosin, which pass through the origin, show clearly that rosin is a truly viscous material.

TABLE IV. VISCOSITY DATA FOR GUM ROSINS

SOURCE	GRADE	DETERMINATIONS	TEMP.	AV. η	MAX. DEVIATION FROM MEAN	AV. φ
			° *C.*	*Poises*	*%*	*Rhes*
American No. 1	N	5	125	2.71	0.74	0.369
		4	140	0.881	0.45	1.135
		4	160	0.299	0.33	3.344
		4	180	0.136	0.73	7.352
American No. 2	N	5	125	4.96	1.41	0.202
		10	150	0.787	0.89	1.27
		4	175	0.225	0.44	4.44
		5	200	0.0906	0.99	11.00
French	WW	4	125	3.55	0.56	0.2814
		4	140	1.33	0.07	0.7502
		4	160	0.384	0.78	2.604
		4	180	0.150	0.67	6.666
Spanish	N	3	125	3.61	0.28	0.277
		4	140	1.29	0.78	0.778
		4	160	0.390	0.77	2.564
		2	180	0.158	1.27	6.329
Portuguese	I	4	125	5.10	0.98	0.1961
		4	140	1.43	1.05	0.7042
		6	160	0.425	0.94	2.353
		4	180	0.167	0.60	5.98
American	D	3	125	9.31	0.54	0.108
		6	150	1.10	0.91	0.909
		3	175	0.268	0.37	3.73
		4	200	0.101	0.99	9.93
Greek	K	3	125	10.07	0.30	0.0993
		5	140	2.420	0.42	0.4129
		5	160	0.596	0.84	1.677
		3	180	0.211	0.00	4.739

TABLE V. RATE OF FLOW–FORCE DATA FOR FF WOOD ROSIN

TEMP.	TIME	PRESSURE	RATE OF FLOW	PRESSURE
° *C.*	*Seconds*	*Cm. Hg*	*Cc./second*	*Grams/cm.²*
130.0	1386.0	47.5^a	0.00289	642
130.0	677.7	98.1^a	0.00590	1326
130.0	464.5	143.7^a	0.00861	1943
130.0	347.2	190.7^a	0.0115	2578
143.2	132.8	189.2^b	0.0301	2558
143.2	192.0	130.6^b	0.0208	1766
153.2	94.7	151.7^c	0.0423	2050
153.2	157.4	92.4^c	0.0254	1249
153.2	251.3	58.6^c	0.0159	792
169.0	175.5	36.6^b	0.0228	495
169.0	83.4	77.2^b	0.0480	1044
169.0	519.6	12.5^b	0.00770	169

[a] At 31.0° C.
[b] At 30.0° C.
[c] At 32.5° C.

Certain trends were noted in the change of viscosity of wood rosins with different treatments. Prolonged heating of wood rosin increased its viscosity. A sample of FF grade, heated for 2 hours at 210° C. and then held at 130° C. for 18 hours, showed a viscosity increase at 150° C. of approximately 5 per cent. Heat-treated FF and I rosins, listed in Tables I and III, have viscosities at this temperature approximately 15 per cent and 5 per cent higher than their respective untreated grades.

Saponification also appears to increase the viscosity of rosins. Two per cent Na_2CO_3 added to I wood rosin increased its viscosity from 0.50 to 1.3 poises at 150° C. All of the limed rosins tested had a much higher viscosity than the original rosins before treatment.

Oxidation of I rosin increased its viscosity tenfold at 150° C.

For the regular untreated wood rosins, the viscosity is lower for rosins of higher acid numbers. Thus, the higher the degree of purification, the lower becomes the viscosity. Abietic acid, which might be expected to have a viscosity lower than any of the wood rosins, has a higher viscosity than both FF and I grades for corresponding temperatures. Oxidation or isomerization of the abietic acid, taking place before or during the viscosity measurement, may account for this.

Such generalities must be restricted in their interpretations. For this discussion, they have been limited to the correlation of different grades of wood rosin produced from material of quite uniform chemical composition by the same carefully controlled process. The comparison is by no means complete nor final but is to be considered as a preliminary attempt of qualitative correlation.

Comparisons on a similar basis are probably not justified with the gum samples obtained from different sources and varying methods of manufacture where considerable fluctuations may exist in the oxidation products, degree of isomerization, residual turpentine, and other factors which may materially affect the viscosity of the particular sample.

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Viscosity-Temperature Characteristics of Rosins

Relations to the Melting Points

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THE EQUATION fixed upon to represent the viscosity-temperature curves of rosin is given by $\log \eta = \log A + b/(T - \theta)$, *where* A *and* θ *are constants approximately the same for all the common American rosins and derivatives studied, and* b *is a constant determining the viscosity of the rosin. The viscosity data are correlated with the so-called melting points as determined by the drop method. The work indicates that the viscosity of many rosins can be estimated, for any desired elevated temperature, from the melting point through use of the formula*

$$\log \eta = \frac{6.05\, t_m - 54}{t - 20} - 3.50,$$

where t_m *(° C.) is the "melting point,"* t *(° C.) is the temperature at which the viscosity is desired, and* $\log \eta$ *is the common logarithm of the viscosity.*

NUMEROUS equations have been suggested to fit the data relating the viscosity of various liquids to the temperature. Some of these have been based upon theoretical considerations, but more often they have been offered as a means of correlating the existing data. With the latter object in view, several of these equations were examined, and attempts made to fit them to the data on rosins as determined by Peterson and Pragoff (*6*).

Madge (*5*) gives the equation:

$$\eta = \frac{A}{T - b}\, exp\,(\beta T)$$

where η = viscosity
T = absolute temperature
A, b, and β = constants
$exp\,(\beta T)$ = e raised to the exponent, βT

This notation is used throughout the following discussion. However, in calculations and constants evaluated, in order to facilitate computation, the exponential function has been taken to be 10 raised to the power in parentheses.

Black (*1*) proposes a hyperbolic function. Hatchek (*3*) reviews the empirical formulas suggested by various investigators. Of interest is a demonstration by Porter (*7*) whereby the available data show that the equation should be of the form:

$$f(\eta) = A + \frac{B}{T}$$

This, however, does not appear to be a limiting condition.

Many investigators (*2*, *4*) have suggested the equation:

$$\eta = AT^{n}\, exp\left(\frac{b}{T}\right) \qquad (1)$$

where b and A = constants
and n is assigned values 0, $^1/_2$, or 1

Andrade (*2*) points out that the equation,

$$\eta = A\, exp\left(\frac{b}{T - \theta}\right) \qquad (2)$$

where θ = additional constant,

holds well for associated liquids.

EXPERIMENTAL DATA

EQUATION TO FIT VISCOSITY DATA. The first equation studied was (1) above. Taking logarithms, it becomes

$$\log \eta - \text{n} \log T = \log A + \frac{b}{T}$$

so that plotting the left hand side against $\frac{1}{T}$ should give a straight line with b as slope. This was done for a number of rosins, where n was first assumed to be zero. The resulting curves approximated straight lines, but no more so than the plot of $\log \eta$ against T. Therefore the equation, in this case, has no merit from an empirical point of view. Changes in the value of n were found not to affect the shape of the curves over the temperature range covered by the data.

Equation 2 was then tried out. Constants were determined for a few of the typical rosins, data for which appear in Table II, by the solution of three simultaneous equations. The constants obtained appear in Table I.

TABLE I. CONSTANT FOR TYPICAL ROSINS

ROSIN	$-\log A$	b	θ
		° *A.*	° *A.*
Wood I	3.34	393	297
Treated B	3.75	672	273
Gum N	3.42	417	297
Treated	4.21	825	276
Greek gum K	4.10	505	299

The data for other rosins were tested graphically, and the following conclusions drawn. The constant, A, is nearly

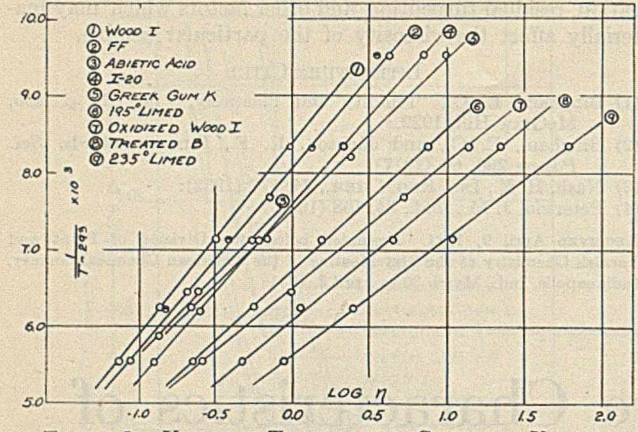

FIGURE 1. VISCOSITY-TEMPERATURE CURVES OF VARIOUS ROSINS

the same for all rosins, excepting treated rosin, abietic acid, Greek gum K, and possibly several other foreign gums. For these rosins it is generally high. For most rosins, A decreases slightly as b increases. The constant, θ, varies from 273 to 300, being somewhat higher for rosins having a low value of b. The only exception is French WW, which gives erratic values of θ, depending on what sets of data are chosen. The term "θ" was therefore fixed at 293, and the data plotted as shown in Figures 1 and 2. The original data, obtained by Peterson and Pragoff (*6*), appear in Table II.

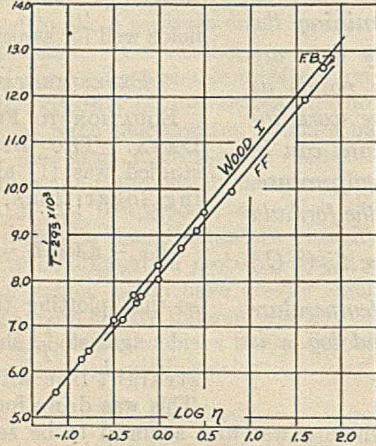

FIGURE 3. VISCOSITY-TEMPERATURE CURVES OF FF AND I WOOD ROSINS

Excepting French WW gum, where a distinct curvature is seen, all points fall fairly closely on straight lines. This is especially true of the ordinary American wood and gum rosins. It then became of interest to discover how far the lines might be extrapolated. A point was therefore determined for I wood rosin at a temperature of 99.1° C. by means of a falling-ball viscometer. The data are given in the last line of Table II, and by the point marked "F. B." of Figure 3.

MELTING POINTS. The results of the above work indicated that the lines might be extrapolated to a lower temperature. The curves for a number of typical rosins were then redrawn to a smaller scale, as shown in Figure 4, and extrapolated in the direction of lower temperature or increasing values for $\frac{1}{T-293}$. The point was then located at which each line crossed the line corresponding to the so-called melting point or softening point, as given in Table II.

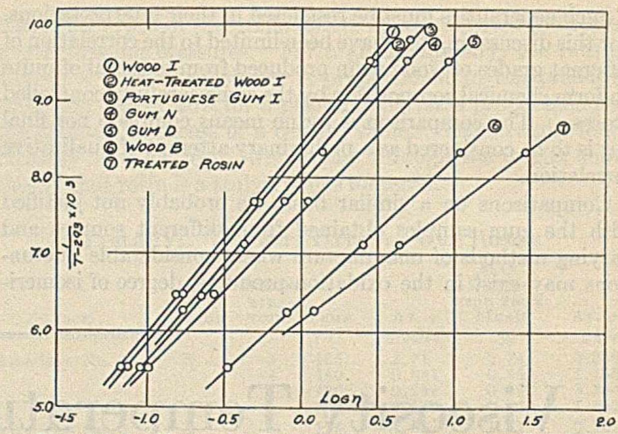

FIGURE 2. VISCOSITY-TEMPERATURE CURVES OF VARIOUS ROSINS

The melting points here used were determined by the thermometer drop method. Between 0.50 and 0.55 gram of rosin was molded about a thermometer bulb $^1/_4$ inch in diameter and $^5/_8$ inch long. The thermometer was then suspended in a test tube $^7/_8$ inch in diameter, and this in turn in a bath maintained at 90° C. If the melting point of the rosin was above 80° C., the bath was maintained at a temperature about 10° above the melting point. The temperature at which the first drop left the end of the bulb was recorded as the melting point. Duplicates usually gave readings agreeing within 1° C.

These melting points, when located on the graph, were found to lie in more or less of a straight line, as shown by the dotted line in Figure 4. Assuming that the extrapolation is trustworthy, the curves show that the melting point is a temperature at which the rosin attains a given viscosity somewhat higher the lower the melting point. According to the graph, the viscosity at the melting point of wood I is about 5000 poises, and about 2000 poises for 235° F. limed rosin. However, using the constants of Table I, the viscosity for treated B at the melting point is calculated to be of the order of 500 poises, whereas the graph gives a value of 2200 poises, and similar figures for many other rosins. Therefore, the data can only fix the order of magnitude of the viscosity at the melting point, though

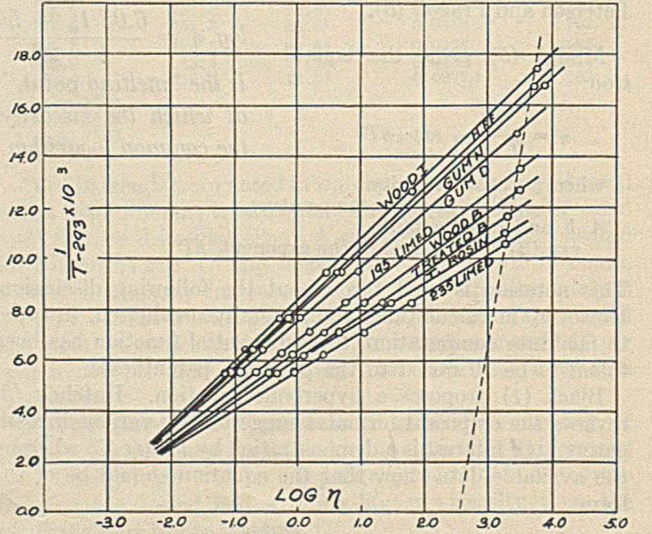

FIGURE 4. VISCOSITY-TEMPERATURE CURVES OF ROSINS, INCLUDING THE MELTING POINTS

it plainly indicates that the viscosity at the melting point is less for a rosin having a higher melting point.

TABLE II. DATA FOR TYPICAL ROSINS

Rosin	η	t	Log η	$\frac{1}{T-293} \times 10^3$
	Poises	*° C.*		$\frac{1}{°A.}$
Wood I	0.960	140	−0.017	8.33
(m. p. = 79.5° C.)	0.317	160	−0.499	7.14
	0.138	180	−0.860	6.25
	0.0728	200	−1.138	5.55
Wood I	2.83	125	0.452	9.52
(m. p. = 77.3° C.)	0.501	150	−0.300	7.69
	0.158	175	−0.801	6.45
	0.0680	200	−1.168	5.56
Wood I-20	7.10	125	0.851	9.52
(m. p. = 84.0° C.)	2.17	140	0.336	8.33
	0.650	160	−0.186	7.14
	0.256	180	−0.591	6.25
	0.126	200	−0.900	5.56
Wood B	11.0	140	1.04	8.33
(m. p. = 98.5° C.)	2.57	160	0.410	7.14
	0.807	180	−0.093	6.25
	0.338	200	−0.471	5.55
Treated wood B	22.08	140	1.358	8.33
(m. p. = 105.5° C.)	4.50	160	0.653	7.14
	1.14	180	0.056	6.25
	0.476	200	−0.322	5.55
Limed, 195° F. (90.6° C.)	6.14	140	0.788	8.33
(m. p. = 93.5° C.)	1.57	160	0.196	7.14
	0.551	180	−0.255	6.25
	0.225	200	−0.647	5.55
Limed, 235° F. (112.8° C.)	63.0	140	1.799	8.33
(m. p. = 114° C.)	11.0	160	1.041	7.14
	2.5	180	0.398	6.25
	0.875	200	−0.057	5.55
Abietic acid	0.549	160	−0.260	8.33
(capillary m. p. = 153° C.)	0.249	175	−0.604	6.45
	0.133	195	−0.877	5.88
Greek gum K	10.07	125	1.000	9.52
(m. p. = 89.5° C.)	2.42	140	0.384	8.33
	0.596	160	−0.225	7.14
	0.211	180	−0.675	6.25
French gum WW	3.55	125	0.550	9.52
(m. p. = 85.0° C.)	1.33	140	0.124	8.33
	0.384	160	−0.416	7.14
	0.150	180	−0.824	6.25
FF	38.09	105	1.59	11.97
(m. p. = 78.0° C.)	6.10	120.5	0.785	9.95
	2.56	130	0.408	9.09
	1.75	134.8	0.243	8.70
	0.965	143.2	−0.015	8.11
	0.630	151.0	−0.200	7.63
	0.559	153.2	−0.252	7.50
	0.392	160.1	−0.406	7.14
Gum D	9.31	125	0.969	9.52
(m. p. = 86.0° C.)	1.10	150	0.041	7.69
	0.268	175	−0.571	6.45
	0.101	200	−0.995	5.56
Treated	29.90	140	1.476	8.33
(m. p. = 109.5° C.)	4.45	160	0.648	7.14
	1.22	180	0.086	6.25
Gum N	4.96	125	0.695	9.52
(m. p. = 79.5° C.)	0.789	150	−0.104	7.69
	0.223	175	−0.652	6.45
	0.096	200	−1.043	5.56
Oxidized wood I	13.83	140	1.141	8.33
(m. p. = 74.0° C.)	5.29	160	0.723	7.69
	0.980	180	−0.009	6.45
	0.261	200	−0.585	5.56
Heat-treated wood I	3.08	125	0.486	9.52
	0.521	150	−0.283	7.69
	0.170	175	−0.769	6.45
	0.0737	200	−1.133	5.56
Heat-treated wood FF	4.23	125	0.626	9.52
	0.724	150	−0.142	7.69
	0.207	175	−0.684	6.45
	0.088	200	−1.055	5.56
Wood I	63	99.1	1.799	11.26

The extrapolation to higher temperatures shows that the lines for each rosin, excepting abietic acid, treated rosin, Greek gum K, and oxidized wood I, pass through a point near to which T is infinity, confirming the conclusion arrived at from the data in Table I that A is about constant. The constant, log A, varies from −3.4 to −3.6, or A varies from 0.00025 to 0.0004 poise.

Extrapolation to temperatures lower than the melting points cannot be safely made. Examination shows that Equation 2 demands that, as the temperature T approaches 293, the viscosity shall approach an infinite value. This is, of course, contrary to observation and serves to prove that the equation breaks down somewhere between the melting point and room temperature.

ESTIMATION OF VISCOSITY FROM MELTING POINTS. If the melting point of a rosin is located on the dotted line of Figure 4, and a line is drawn through this point and the point

$$\frac{1}{T-293} = 0, \log \eta = -3.5$$

any point on the line thus drawn determines the viscosity of the rosin for the corresponding temperature. The assumptions involved in this procedure are obvious.

Assuming that all rosins have the same constant, A, and that all points representing the viscosity at the melting point lie on the dotted line, a simple formula for the viscosity of a rosin can be derived. Let y stand for the variable, $\frac{1}{T-293}$ or $\frac{1}{t-20}$, where t is in ° C., and x for log η. The dotted line can then be represented by

$$x = 2.55 + 67\,y \tag{3}$$

and the viscosity line for any particular rosin by

$$x = -3.5 + by \tag{4}$$

The melting point, x_m, y_m, is common to both lines. Putting these in Equations 3 and 4, and eliminating x_m between them, an equation is obtained involving the four constants and y_m. Solving for b and substituting $\frac{1}{t-20}$ for y, $\frac{1}{t_m-20}$ for y_m, and log η for x, the following equation is obtained:

$$\log \eta = \frac{6.05\,t_m - 54}{t-20} - 3.5 \tag{5}$$

From the equation, given the melting point, t_m, an approximate viscosity may be calculated for any temperature t (in ° C.). This has been done for a number of typical rosins. The values are given in Table III, together with the observed viscosities.

TABLE III. MELTING POINTS AND VISCOSITIES OF TYPICAL ROSINS

Rosin	t	η	
		Obsvd.	Calcd.
	° C.	*Poises*	*Poises*
Wood I	99.1	63	55
	125	2.83	2.8
	150	0.501	0.49
	200	0.0680	0.063
Limed, 235° F. (112.8° C.)	140	63	61
	160	11	11
	180	2.5	2.9
	200	0.875	1.0
Treated wood B	140	22.8	22.9
	160	4.50	4.68
	180	1.14	1.40
	200	0.476	0.55
Heat-treated FF	125	4.23	3.7
	150	0.724	0.76
	175	0.207	0.20
	200	0.0880	0.076
Gum N	125	4.96	3.7
	150	0.787	0.76
	175	0.223	0.20
	200	0.0906	0.076
Gum D	125	9.31	9.5
	150	1.10	1.3
	175	0.268	0.34
	200	0.127	0.125
Treated	140	29.90	37
	160	4.45	7.0
	180	1.22	2.0

The data on the last three rosins illustrate clearly the adaptability and limitations of the formula. The melting points of gum N and gum D do not lie on the dotted line of Figure 4; nevertheless the agreement between the calculated and observed values of viscosity is fairly good. On the other hand, treated rosin, although a straight line, does not fit with the formula. Several foreign gums also deviate widely from the calculated values.

Conclusions

The equation

$$\eta = A\ exp \left(\frac{b}{T - \theta}\right) \qquad (2)$$

fits all rosins investigated (eighteen altogether) with good agreement over the temperature range 100° to 200° C.

The constant θ, excepting for French WW, is about the same for all rosins studied, and varies from 273 to 300. The constant log A is approximately the same for most rosins, varying from -3.4 to -3.6 when $\theta = 293$.

Extrapolation of the lines obtained in this way can be extended to the so-called melting point of the rosin, to estimate the viscosity at this temperature. It appears to be of the order of 5000 poises.

The constant b of Equation 2 determines the viscosity of the ordinary American gum or wood rosins. From this, an expression may be derived which gives the approximate viscosity of a rosin at any desired temperature. It is:

$$\log \eta = \frac{6.05\ t_m - 54}{t - 20} - 3.50$$

where t_m = melting point, ° C., as determined by drop method
t = temperature, ° C., at which viscosity is desired
$\log \eta$ = common logarithm of viscosity in poises.

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Parallel Scale Charts

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Recently the authors were called upon to make a large number of calculations of boiler feed-water treatments, employing soda ash and lime as water-softening agents. The calculation of the necessary amounts of soda ash and lime in each case was made by using modifications of equations originally developed by Stabler (*1–4*). In the original Stabler formulas the amounts of the various positive and negative radicals, such as calcium, magnesium, carbonate, and bicarbonate found by analysis of the water, were expressed in parts per million. The number of parts per million of each positive or negative radical was then multiplied by its own so-called reaction factor, and the algebraic sum of these products was in turn multiplied by a conversion factor to give the amount of soda ash, or soda ash and lime, necessary for softening the water. The result was expressed in ounces per thousand gallons.

In the waters analyzed here, iron, aluminum, carbonate, and hydrogen ions were present in such negligible amounts that these radicals were omitted from the calculation, and the formulas were modified as follows:

Soda Ash Treatment. (To be used for a water containing a large amount of calcium but only a small amount of magnesium).

$$\text{Ounces soda ash per 1000 gallons water} = 7.44\ (r_1\text{Ca}) \qquad (1)$$

Lime and Soda Ash Treatment. (To be used for a water containing a moderate or large amount of magnesium in addition to calcium.)

$$\text{Ounces soda ash per 1000 gallons water} = 7.44\ (r_1\text{Ca} + r_2\text{Mg} - r_3\text{HCO}_3) \qquad (2)$$

$$\text{Ounces lime per 1000 gallons water} = 4.16\ (r_2\text{Mg} + r_3\text{HCO}_3) \qquad (3)$$

where Ca = p. p. m. of calcium $r_1 = 0.0499$
Mg = p. p. m. of magnesium $r_2 = 0.0822$
HCO_3 = p. p. m. of bicarbonate $r_3 = 0.0164$

By substituting the numerical values of r_1, r_2, and r_3 in the above equations and multiplying through by the coefficient in front of the parentheses, the following are obtained:

$$\text{Ounces soda ash} = 0.371\ (\text{p. p. m. Ca})\ (\text{soda ash treatment}) \qquad (1)$$

$$\left.\begin{aligned}&\text{Ounces of soda ash} = 0.371\ (\text{p. p. m. Ca}) + 0.612\ (\text{p. p. m. Mg}) - 0.122\ (\text{p. p. m. HCO}_3) && (2)\\ &\text{Ounces of lime} = 0.342\ (\text{p. p. m. Mg}) + 0.068\ (\text{p. p. m. HCO}) && (3)\end{aligned}\right\}\ (\text{soda ash and lime treatment})$$

Considering Equation 1, it is obvious that the amount of soda ash is a direct function of the number of parts per million of calcium to be removed, and that a pair of parallel scales can be laid out in which each part per million of calcium will correspond to 0.371 ounce of soda ash. Thus by knowing the amount of calcium in parts per million, one reads directly across to the correct amount of soda ash.

Equation 2 is applied visually by using the two scales described above, and in addition a scale for the amount of magnesium and one for the amount of bicarbonate. Each part per million of magnesium is made to correspond to 0.612 of a division of the soda ash scale. On the bicarbonate scale each part per million of bicarbonate corresponds to 0.122 of a division of the soda ash scale.

By means of these four scales placed side by side, Equation 2 can now be evaluated as follows: A straight edge is placed upon the amount of calcium and the corresponding amount of magnesium noted. To this amount is added the number of parts per million of magnesium actually found by analysis. The straight edge is then moved upward to the point representing the sum. The amount of bicarbonate corresponding to this sum is noted and from this amount is subtracted the number of parts per million of bicarbonate found by analysis. The straight edge is then moved downward to the point

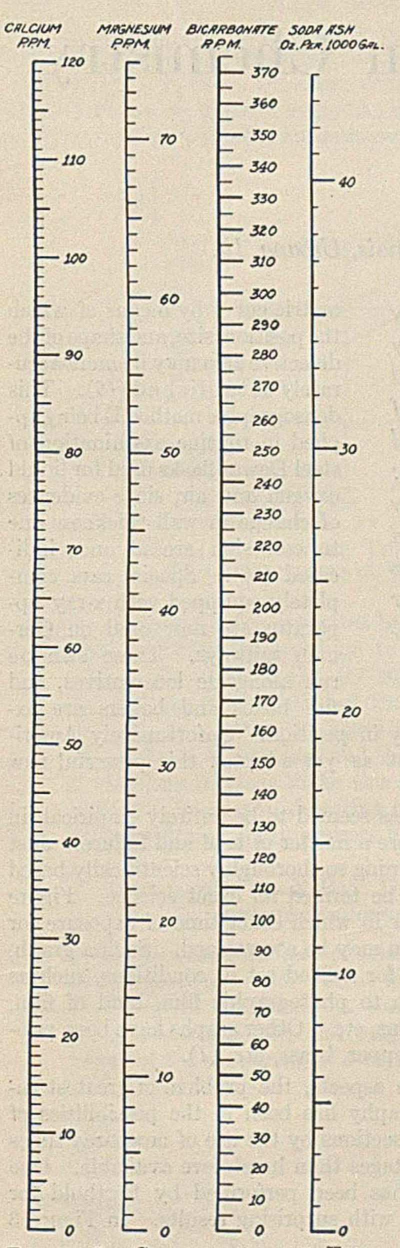

FIGURE 1. CALCULATION FOR FEED-WATER TREATMENT WITH SODA ASH

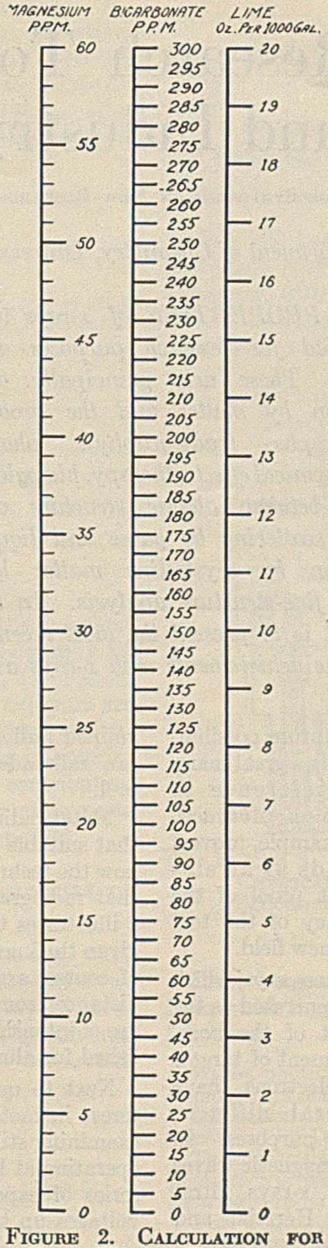

FIGURE 2. CALCULATION FOR FEED-WATER TREATMENT WITH LIME

representing the remainder. The amount of soda ash corresponding to this point is the correct amount to be used with the lime in the soda ash and lime treatment.

If the amount of bicarbonate actually found by analysis is greater than the "bicarbonate equivalent" of the calcium and magnesium, no soda ash is necessary.

Scales for the application of Equation 3 are constructed in a similar manner and the correct amount of lime is found visually. The various scales described are shown in Figures 1 and 2.

The authors realize that the application of these particular formulas is very limited, and that the effectiveness of the amounts of water-softening materials calculated by their use is a matter of controversy. However, the authors do wish to call particular attention to the fact that parallel scale charts of the above type can be used to advantage many times in the chemical calculations where the equation is of the general type:

$$K_1(K_2X + K_3Y + K_4Z\ldots.) = U$$

where K_1, K_2, K_3, and K_4 are constants and X, Y, Z, and U are variables.

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RECEIVED September 14, 1931.

An Efficient Gas-Liquid Reaction Tower

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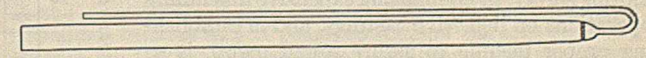
THE accompanying figure shows a simple reaction tube which is especially adapted to procedures involving reactions between gases and liquids.

To a Büchner type funnel containing a "gerate" glass plate, are sealed the tower and the gas lead. These funnels are available in Jena glass in three standard porosities (3 to 5μ, 5 to 7μ, less than 7μ), and under a small gas pressure they give a spray of tiny bubbles. This results in a large reaction surface per volume of gas used. Since the funnels are obtainable in different sizes, the towers may be small or large, according to the requirements of the reaction under consideration.



REACTION TOWER

Towers of this type have proved very satisfactory in oxidation experiments with oxygen gas in this laboratory.

RECEIVED January 2, 1932.

X-Rays as a Research Tool in Chemistry and Industry

[PART OF SYMPOSIUM ON NEW RESEARCH TOOLS]

GEORGE L. CLARK, *Department of Chemistry, University of Illinois, Urbana, Ill.*

THE PROPERTIES of x-rays which may be applied for research purposes are briefly reviewed. These are, principally: differential absorption by matter and the production of shadowgraphs (radiography); photochemical effects (chemical effects, therapy, biological effects); relation between atomic structure and x-ray spectra; scattering by gases and liquids; and diffraction by crystalline matter leading to ultimate fine-structure analysis. In this paper the effort is to present the most recent and entirely new achievements with x-rays as a tool.

X-RAYS have been known now for thirty-six years, and their production, properties, and wide application are generally familiar. And yet they very properly may be classed as a new research tool, since the full possibilities of x-ray science are still undreamed of, and since new achievements are being recorded daily. It is the purpose of this brief paper to select a few of the most recent actual developments in the use of radiation as a research tool, rather than to enumerate and indicate the general status of progress or the future possibilities. Each of the examples selected from among a great many (as reference to *Chemical Abstracts*, for example, proves) stands as an eloquent proof of the efficacy of the tool in a new field.

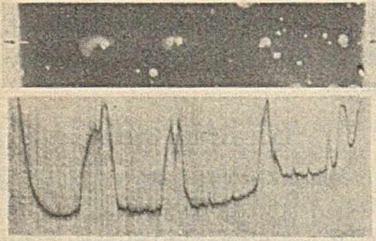


FIGURE 1. RADIOGRAPH OF DEFECTIVE STEEL

These rays, which are generated as the result of the bombardment of targets by electrons, have several different properties which may be utilized for research purposes. In charts drawn to represent the range of electromagnetic waves —including cosmic rays, γ-rays from radium, x-rays, ultraviolet rays, visible light, infra-red rays, and Hertzian and radio waves—x-rays run from 0.06 to 1019 Å. In the usual applications, however, wave lengths above 1.5 Å. are not commonly employed.

From researches in various fields the following have been somewhat arbitrarily selected to indicate the status and possibilities of x-rays as a tool.

ADVANCES IN INDUSTRIAL RADIOGRAPHY

The chief interest here lies in the examination of metal specimens for gross structure and imperfections by the same technic applied in medical diagnosis of broken bones, foreign bodies, internal tumors, etc. The value of this method in promoting safety, in eliminating expensive machining operations on defective castings, and in establishing proper technic to assure sound metal, is so generally well known that comment is scarcely required. Numerous industries have installed x-ray plants as necessary equipment. Figure 1 shows a typical radiograph of defective steel, together with a quantitative microphotometric curve by means of which the position, size, and shape of the defective area may be more accurately established (*15*). This densographic method is being applied in routine examination of steel Dewar flasks used for liquid oxygen and air, since evidences of change in wall thickness due to corrosion are at once indicated (*16*). Special cars completely equipped with x-ray apparatus are now used on German railways. These can be run alongside locomotives, and fire boxes and boilers are examined radiographically in position. Unfortunately American railroads have not as yet adopted this powerful new tool.

Metal radiography has seemed to be entirely empirical, in that suitable results were a matter of trial and failure. Just now the technic is becoming so thoroughly scientifically based that radiography may be termed an exact science. Figure 2 illustrates the manner in which exact time of exposure for given thicknesses of iron may be ascertained. Such a graph, of course, applies only for a fixed set of conditions, such as distance from specimen to photographic film, kind of film, use of intensifying screens, etc. Other graphs have been published for aluminum, copper, brass, etc. (*1*).

Next to quantitative aspects, the problem of greatest interest in metal radiography has been in the possibilities of examining still thicker sections by the use of new x-ray tubes operating at higher voltages than heretofore available. One series of experiments has been performed by Berthold for voltages up to 350 kv. with surprising results. In Figure 3

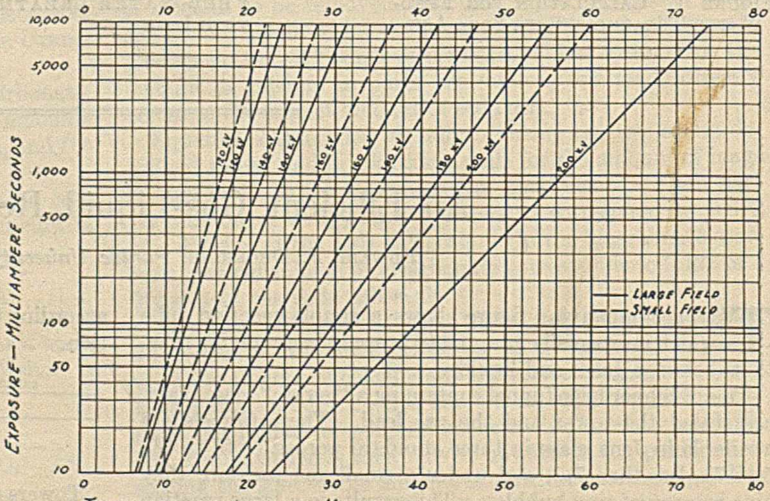


FIGURE 2. GRAPH FOR ASCERTAINING EXPOSURE TIME FOR GIVEN THICKNESSES OF IRON

is plotted the thickness of iron penetrated *vs.* voltage. Instead of going up nearly linearly with voltage, the curve flattens markedly. Evidently little is to be gained therefore in going above 250 kv. Of course commercial x-ray tubes for higher voltages are not now available, and some of the impetus for building high potential tubes is removed by these results

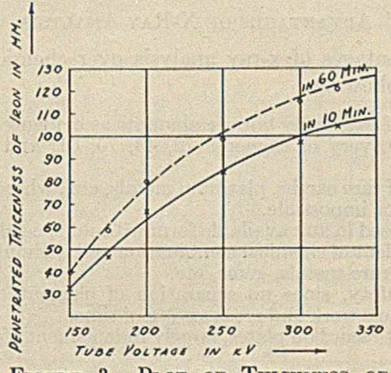


FIGURE 3. PLOT OF THICKNESS OF IRON PENETRATED *vs.* VOLTAGE

In this connection, mention must be made of the ingenious application of γ-rays from radium to metal radiography by Mehl and his associates (*14*). By this method, 11 or more inches of steel are penetrated, but the times of exposure are of course very long—from 12 hours up. However, the extreme simplicity of the method and the possibility of examining iron structure in place make this a distinct contribution to the science. Successful detecting of defective stern posts in new United States Navy cruisers has been reported.

RECENT APPLICATION OF X-RAY DATA TO THEORIES OF ATOMIC STRUCTURE

With the increasing number of triumphs of the new wave mechanics in physics, much weight is being placed in x-ray researches of great precision. A complete survey of these developments is impossible, and only a single experimental study—that of the scattering of x-rays by gases—is selected.

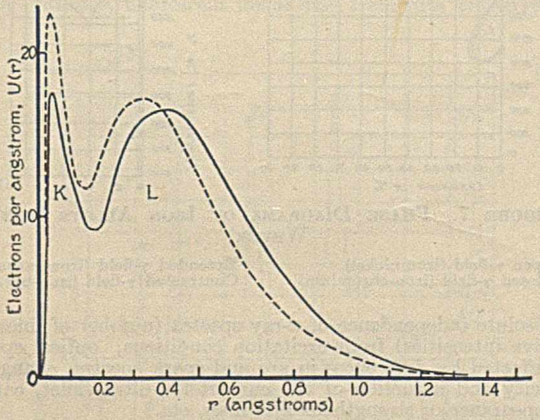


FIGURE 4. RADIAL ELECTRON-DISTRIBUTION CURVES OF NEON GAS, DETERMINED FROM EXPERIMENTS ON X-RAY SCATTERING

Solid line, neon from experiment; broken line, Na^+ from wave mechanics (*19*)

One of the most promising recent developments in physics has been the use of data from the scattering of x-rays by gases to determine electron distribution in atoms and to test data calculated from wave mechanics. Compton (*9*) has shown that the density of electrons is represented by a Fourier integral of the form:

$$U(r) = Zr\int_0^\infty B\sin(\pi r x)dx$$

where $U(r)$ = number of electrons per Å. at distance r from center
Z = atomic number
B (depending on intensity of scattering) $= 2\pi x\left(\frac{S-1}{Z-1}\right)^{1/2}$
where S = scattering per electron at $x = 4/\lambda \sin(\phi/2)$

Wollan (*19*) has determined the distribution in helium, neon, and argon, and found the curves for $U(r)$ against r in good agreement with similar curves derived from wave mechanics. For neon the data actually are able to separate the K and L electrons, as shown in Figure 4.

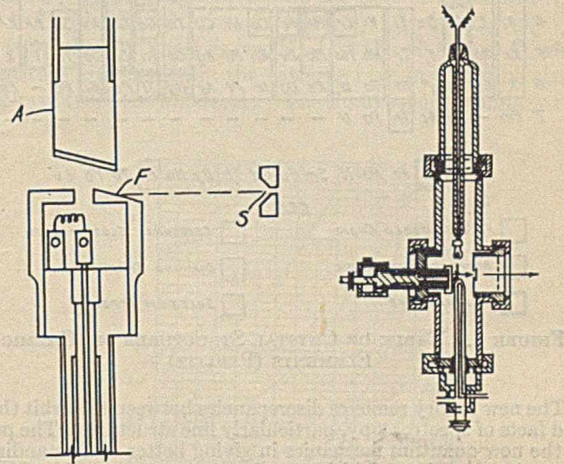


FIGURE 5. TWO NEW TYPES OF X-RAY TUBES FOR CHEMICAL ANALYSIS BY MEANS OF FLUORESCENT SECONDARY X-RAYS

Left, Hevesy; right, Stintzing

Heisenberg cites as the most important experiments, from which may be induced concepts of present physics, the following:

> Wilson photographs by the cloud-track method, showing that α and β rays may be regarded as streams of minute particles.
>
> Diffraction of β rays, or electrons showing wave-like properties discovered by Davisson and Germer in 1927.
>
> The diffraction of x-rays showing form of wave motion, and the photoelectric ejection of electrons, when x-rays strike matter, showing corpuscular properties.
>
> The Compton-Simon experiment in which x-rays passing through supersaturated water vapor are scattered by molecules, producing both recoil electrons and photoelectrons, the first by a collision of a photon (light particle) with an electron in a molecule, and the second as a result of the collision of this photon moving in a new direction with a second molecule.
>
> Collision experiments of Franck and Hertz leading to the conclusion that atoms in a gas through which a beam of slow electrons passes can assume only discrete energy values and "stationary states" as originally postulated by Bohr.

In simplest terms the essential facts involved underlying the new theories which have displaced the Bohr model are as follows:

> Matter, including free electrons, and radiation possess a remarkable duality of character, as they sometimes exhibit the properties of waves, and at other times those of particles. A thing cannot be a form of wave motion and composed of particles at the same time. It is experimentally certain only that light sometimes behaves as if it possessed some of the attributes of a particle, but there is no experiment which proves that it possesses all the properties of a particle; similar statements hold for matter and wave motion.
>
> Language is incapable of describing processes occurring within atoms, for it was invented to express the experiences of daily life which consist of processes involving exceedingly large numbers of atoms. Furthermore it is almost impossible to modify lan-

guage so as to describe these atomic processes, for words can only describe things of which mental pictures can be formed, and this ability is a result of daily experience. Mathematics is not subject to this limitation.

Contradictions between theory (Bohr) and experiment have led to the necessity of demanding that no concept enter a thing which has not been experimentally verified.

The principle of uncertainty shows, among other things, that the position and velocity of an electron (in an orbit, for example) cannot be known simultaneously. Determinism is dropped out of the latest formulations of theoretical physics.

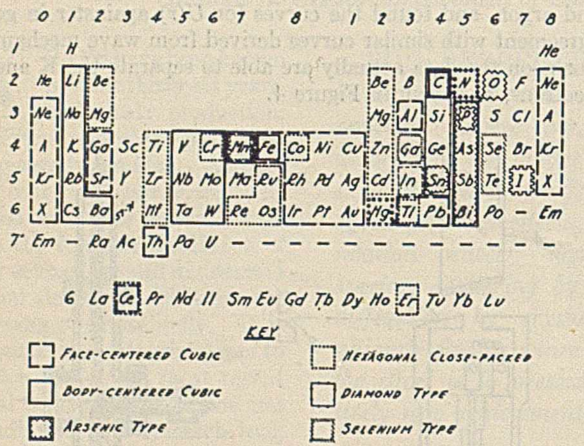


Figure 6. Table of Crystal Structures of Chemical Elements (Perlitz)

The new theory removes discrepancies between the orbit theory and facts of spectroscopy, particularly fine structure. The power of the new quantum mechanics in giving better understanding of events on atomic scale is becoming increasingly evident. The structure of the helium atom, the existence of half-quantum numbers in band spectra, the continuous spatial distribution of photoelectrons, and the phenomenon of radioactive disintegration are items which baffled old theories but are successfully achieved by the new.

As nearly as may be visually conceived, the new model of the atom spreads the electron from a point charge moving in orbits to diffuse shells of negative electricity with increasing density, the closer to the nucleus. Hence the orbits are smudged, in the words of G. P. Thomson, but the electrons retain, in a sense, their individuality. However, Dirac regards waves or particles of light or electrons as two useful abstractions for describing the same physical reality, but he warns the student against combining them into a mechanism that behaves like familiar things.

The Bohr atom is, therefore, welcomed today as an indispensable model, expected to remain so for many years to come, and admitted to be inadequate. Even the most advanced mathematical physicists still speak of "orbits" and "electron jumps." Nor has the final word been said with the new mathematical models.

Finally, in the words of Jeans, "the Great Architect of the Universe now begins to appear as a pure mathematician."

Chemical Analysis from X-Ray Spectra

Since definite x-ray wave lengths, both emission and absorption, are characteristic of the chemical elements, it follows that x-ray spectroscopy may find practical application in qualitative and quantitative analysis. The Moseley law, of course, is of splendid assistance, more particularly in the qualitative discovery of new elements in complex mixtures, since the wave lengths for these elements may be accurately predicted.

The five general procedures employed in analysis are as follows:

(1) Measurement of primary spectral emission lines (K or L or M series), in which the unknown substance undergoing analysis is made the target of an x-ray tube.

(2) Measurement of secondary fluorescent emission lines in which the unknown is placed on some device inside of the x-ray tube so that it is screened from the cathode rays but directly irradiated by the primary x-ray beam.

(3) The same except that the unknown is irradiated outside of the x-ray tube; on this account the intensities are greatly decreased and the time increased.

(4) Measurement of characteristic absorption-edge wave length in which the unknown serves as an absorbing screen.

(5) Use of a cathode-ray tube with thin windows for passage of rays, with bombardment of unknown outside and spectrographic analysis of x-rays generated.

Advantages of X-Ray Analysis

The advantages of x-ray analysis over chemical methods are in the following:

Analysis of extremely minute amounts as evidenced by the triumph of discovery of elements 72, 43, 75, 61, and 87 (Papish, 1931).

Analysis of rare earths, platinum metals, etc., where separations are difficult or impossible.

Material used in any available form without special preparation and independent of chemical combination and without loss; hence valuable for rare metals, gems, etc.

Greater safety, since no separation of elements is involved; hence much less work and great saving of time.

Permanent record on plates, largely independent of the personal equation.

The advantages of x-ray analysis over optical spectroscopy lie in the following:

The great simplicity of x-ray spectra, particularly the K series emission, as compared with the great complexity of optical spectra (notably iron).

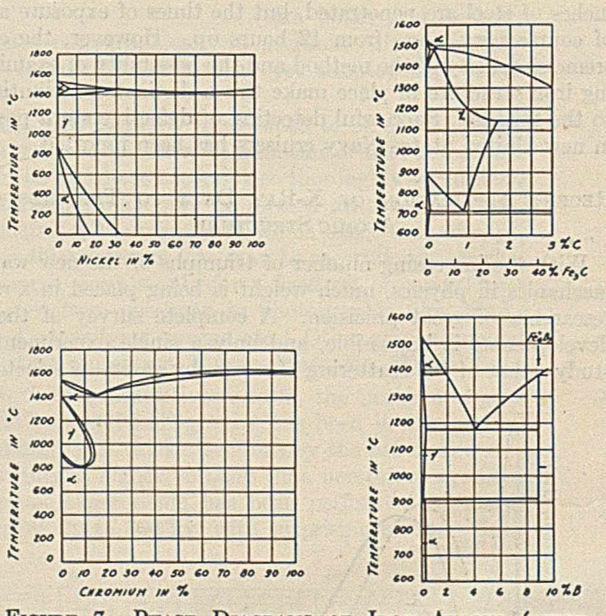


Figure 7. Phase Diagrams of Iron Alloys (after Wever)

Open γ-field (iron-nickel)	Extended γ-field (iron-carbon)
Closed γ-field (iron-chromium)	Contracted γ-field (iron-boron)

Absolute independence of x-ray spectra (number of lines and relative intensities) from excitation conditions; optical spectra are affected by differences in arc and spark spectra, changes in capacity and induction of the current for ultra-violet, causing disappearance or strengthening of lines, etc.

Independence of x-ray spectra from chemical combination or valence, since only atoms and not molecules are involved: optical spectra are affected by kind of chemical combination, band spectra of molecules, presence of foreign substances, etc.

Disadvantages of X-Ray Spectra

The disadvantages in the use of x-ray spectra are as follows:

They cannot be used for analysis of the lightest elements, since characteristic wave lengths are too long for measurement by the usual crystal grating; the practical limit is calcium ($Z = 19$).

Somewhat expensive and special equipment is necessary and much of it commercially available only in Europe.

Very special technic is essential, including selection of proper voltage, etc., for accurate quantitative analysis.

Somewhat limited accuracy for quantitative work involving comparison of line intensities with standards. The line intensities are not proportional strictly to the weight proportions of elements in the preparation, for several reasons noted below.

The selective volatilization of constituents of mixture from focal spot of target for primary emission method gives erroneous results; this difficulty is partly alleviated by rotating the anode in order to present fresh surface, or by using the fluorescent spectra methods.

	I		II		III		IV		V		VI		VII		VIII			
	a	b	a	b	a	b	a	b	a	b	a	b	a	b	a			b
I														1 H				2 He
II	3 Li ▲		4 Be ●			5 B ○		6 C □		7 N □		8 O		9 F				10 Ne
III	11 Na ▲		12 Mg ▲			13 Al ●		14 Si ●		15 P ●		16 S ○		17 Cl				18 Ar
IV	19 K ▲		20 Ca ▲		21 Sc		22 Ti ●		23 V ●		24 Cr ●		25 Mn ■		26 Fe	27 Co ■	28 Ni ■	
		29 Cu □		30 Zn □		31 Ga		32 Ge ●		33 As ●		34 Se		35 Br				36 Kr
V	37 Rb ▲		38 Sr ▲		39 Yt		40 Zr ○		41 Nb ●		42 Mo ●		43 Ma		44 Ru ■	45 Rh ■	46 Pd ■	
		47 Ag ▲		48 Cd ▲		49 In		50 Sn ●		51 Sb ●		52 Te		53 I				54 X
VI	55 Cs ▲		56 Ba ▲		58 Ce ○		72 Hf		73 Ta ●		74 W ●		75 Re		76 Os ■	77 Ir ■	78 Pt ■	
		79 Au □		80 Hg ▲		81 Tl ▲		82 Pb ▲		83 Bi ▲		84 Po		85 —				86 Em
VII	87 —		88 Ra ▲		89 Ac		90 Th		91 Pa		92 U							

■ OPEN γ-FIELD
● CLOSED γ-FIELD
□ EXPANDED γ-FIELD
○ CONTRACTED γ-FIELD
▲ INSOLUBLE

FIGURE 8. PERIODIC ARRANGEMENT OF ELEMENTS SHOWING TYPE OF BINARY ALLOY WITH IRON (AFTER WEVER)

Great decrease in intensities and prolongation of time for fluorescent spectra methods.

A serious difficulty for quantitative analysis is the effect of absorption edges on emission lines; if in a mixture one element has one characteristic absorption edge of longer wave length than the emission lines of other constituents of the mixture, these lines will be selectively absorbed. Such difficulties are avoided, when standardizing substances are used, by not mixing but by using a rotating target with the samples contiguous and excited to emission separately but, of course, registering on the same photographic plate. The effect of the absorption edges of silver and bromine in the plate must be taken into account also.

Line coincidence (*11*) may occur and cause difficulties; these are avoided only by greater resolution of spectra and use of higher orders of reflection.

There appear certain foreign lines, such as mercury from the diffusion pump, tungsten from metal sputtered in the target from the hot cathode, fluorescent metal lines from slits, traces of material from previous experiments on the surface of the anode, etc.; these can be checked with blank runs of apparatus.

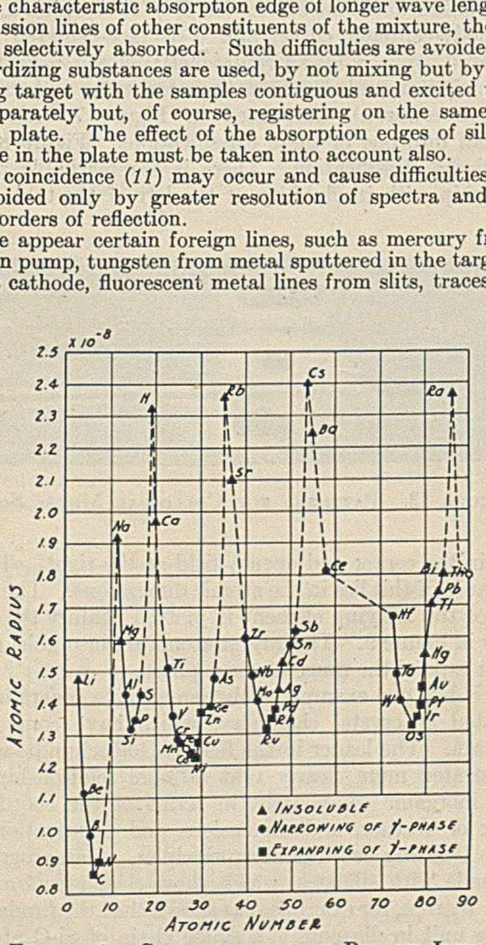


FIGURE 9. CLASSIFICATION OF BINARY IRON ALLOYS AS A FUNCTION OF ATOMIC RADIUS (AFTER WEVER)

In certain mixtures, characteristic rays of one element can be excited by the characteristic rays of another element and thus produce a strengthening of intensity of lines for the first. Gunther, Stransky, and Wilcke observed that a mixture of chromium and copper in the ratio of 46:54 appeared to have the ratio 60:40 of characteristic rays of chromium excited by copper rays. Dilution with ground quartz produced true results.

There is varying sensitivity of the photographic emulsion to different wave lengths; long wave lines are blacker in proportion to intensity than shorter ones.

Of special interest at the present time, because of new developments which meet serious defects for quantitative analysis, are the fluorescent-ray methods. Several new types of tubes have been designed, among the best of which are those due to Hevesy and Stintzing (Figure 5). In the Hevesy type the substance for analysis is placed on the platform, *F*, which is entirely screened from the cathode rays but may be struck by x-rays from the anode, *A*. The fluorescent secondary rays are then spectrographically analyzed through the slit, *S*. In the Stintzing type, electrons from the hot filament strike on the vertical anode with cone-shaped top, the whole anode being rotated by means of the pulley shown at the bottom, in order to present continually renewed surfaces and thus permit large energies. The substance for analysis is pasted on the plate at right angles to the anode axis, and this so-called fluorescent anode is also rotated. The secondary beam passes out through a window and may be analyzed. For qualitative analysis of materials most of the disadvantages listed above are unimportant and, with the advent of high-power tubes producing very intense radiation, the fluorescent method has become most important. For quantitative analysis Hevesy (*13*) has made a very careful study of the factors determining the results which can be obtained. Characteristic primary rays ordinarily give six or seven times more intense secondary rays than rays with a continuous spectrum. For greatest intensity a metal must be chosen for target whose characteristic rays are 0.15–0.20 Å. shorter than the absorption bands of the elements undergoing analysis.

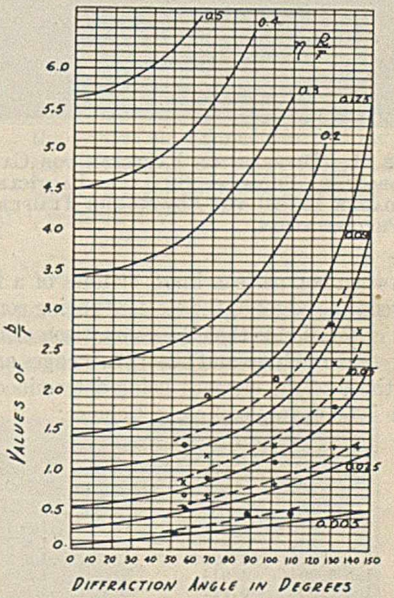


FIGURE 10. CURVES FOR DETERMINATION OF GRAIN SIZE IN COLLOIDAL RANGE FROM BREADTH OF X-RAY DIFFRACTION INTERFERENCES (2)

Especial attention also has been paid to the distorting effects upon emission-line intensity of absorption edges of a foreign

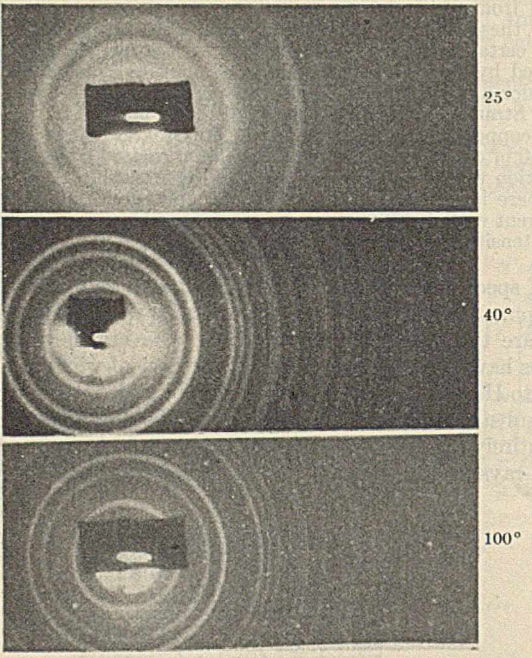


Figure 11. Diffraction Patterns for Cadmium Hydroxide, Showing Smaller Particle Size (Broader Lines) the Lower the Temperature of Precipitation

element between comparison lines, or lines of a foreign substance between the edges of the elements being compared, etc. The general conclusion is that the comparison element should be chosen so that the lines and absorption edges are as near as possible to those of the element being determined. The following table is an example of correct choice:

Element Analyzed	Line λ Å.	Edge λ Å.	Comparison Element	Line λ Å.	Edge λ Å.
Pt	$L\alpha_1$ 1.310	1.070	Ta	$L\beta_3$ 1.303	1.058
In	$L\alpha_1$ 3.764	3.313	Cd	$L\beta_1$ 3.730	3.322
Cd	$L\alpha_1$ 3.948	3.496	Ag	$L\beta_1$ 3.927	3.505
Mo	$L\alpha_1$ 5.394	4.914	Nb	$L\beta_1$ 5.480	5.012
Rb	$L\alpha_1$ 7.303	6.941	Si	$K\alpha_1$ 7.109	6.731
Ge	$K\beta_1$ 1.126	1.115	Ta	$L\alpha_1$ 1.135	1.112
Zn	$K\beta_1$ 1.293	1.281	Hf	$L\beta_2$ 1.324	1.293
Ni	$K\beta_1$ 1.497	1.489	Er	$L\beta_2$ 1.511	1.480
Ti	$K\beta_1$ 2.509	2.494	Cs	$L\beta_2$ 2.506	2.466
S	$K\beta_1$ 5.021	5.012	Mo	$L\beta_2$ 4.909	4.904
Al	$K\beta_1$ 7.941	7.947	Br	$L\beta_1$ 8.108	7.727
Mg	$K\beta_1$ 9.535	9.511	As	$L\beta_1$ 9.394	9.300

Fortunately the distorting effect is appreciable only when there is a considerable amount of a foreign element present; in ordinary cases it may be neglected without seriously affecting the quantitative analysis. An important application of secondary-ray analysis is that of complex minerals down to 0.1 per cent of a constituent of even 0.001 mg. of any element. Another is in tests of preparations for purity, in which concentration of impurities of 1 part in 10,000 may be found. Eddy, Laby, and Turner (*10*) were able to find 1 part of iron in 300,000 parts of zinc.

Figure 12. Pattern for Supposed Dimethyl Barium Carbonate (Above) and Pure Barium Carbonate

High-Powered X-Ray Tubes and Researches with X-Rays of Great Intensity

The tremendous improvement in the design and construction of x-ray diffraction tubes for fine-structure examination of materials is a recent development of greatest significance. Among these new features, the line and cross focus filaments for cathodes has enabled the distribution of large energy over an appreciable surface of the target, but the adjustment is such that the energy appears to come from a point source or focal spot. The great advantage in studying crystalline structures of changing systems, unstable compounds, living tissues, etc., practically as a series of motion pictures, has been outlined fully in a recent paper by Clark and Corrigan (*5*) and need not be repeated here.

Crystalline Structures of the Elements

The present status of crystal-structure determination of the chemical elements is diagrammatically represented in Figure 6, from which periodic relationship, allotropic modifications, and remaining gaps are clearly indicated.

Systematization of Iron Alloys and Other Inorganic Systems

The structures of the alloys of iron have seemed to be almost hopelessly unrelated and unpredictable. However, as the result of excellent researches in the laboratories of Westgren, Wever, and others, generalizations may now be made with certainty. Wever classes the alloys into four groups depending upon the effect of the foreign element upon the polymorphic transitions of iron (α, β, γ, δ, of which α, β, and δ are body-centered cubic, and γ is face-centered cubic). These are: open γ-field (iron-nickel); closed γ-field (iron-chromium); expanded γ-field (iron-carbon); and narrowed γ-field (iron-boron), illustrated in Figure 7. All binary alloys fall into one of these classifications. Figure 8 shows the periodic classification. There is a remarkable periodic relationship with insolubility at the left of the table, closed γ-field in the center and open γ-field at the right. The real significance of this lies in the atomic dimensions. The atomic radius of the alloying element is plotted against the atomic number in Figure 9. The largest atoms are insoluble, and the smallest expand the range of the γ-phase.

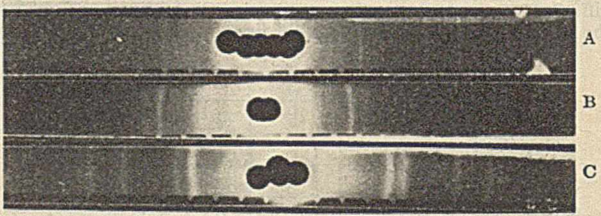


Figure 13. Patterns for Colloidal Metal Sols

This is but one example of the remarkable generalizations, designated as crystal chemistry, which have come out of x-ray data. The leader in the field is Goldschmidt, who has demonstrated more clearly that rational relationships exist among inorganic compounds, in terms of the coördination number of Werner, and dimensions and polarization properties. Utilizing coördination principles, great progress has been made with silicates, which show clear structural relations. Warren, for example, has shown that the fundamental building unit in diaspore is a single chain of Si-O atoms, in asbestos a doubled chain, and in mica a sheet of adjacent chains.

Grain-Size Measurement in Colloidal Range

It has been known for some time that x-ray diffraction interference becomes broader as the grain size of particles decreases below 10^{-5} to 10^{-6} cm. Numerous equations connecting grain size and width of the interferences at points of half-maximum intensity have been proposed. Brill (*2*) has carried the matter farthest in showing that the shape of colloidal particles may be deduced. Figure 10 represents a series of standard curves plotted by Brill for b/r against the diffraction angle, χ, where b is the measured width of the interference and r is the radius of the samples. Interpolation gives the position on curves for various values of $\eta\ R/r$, where R is the radius of the camera and η is a number defined by

$$\eta = \frac{1}{3.6\pi}\left[B\ \cos\frac{\chi}{2} - \frac{I}{B}\left(\pi\ \frac{r}{R}\right)^2 \cos^3\frac{\chi}{2}\right]$$

or for the cubic system,

$$\eta = \frac{\lambda}{4\pi a}\sqrt{\frac{(h/m_1)^2 + (k/m_2)^2 + (l/m_3)^2}{h^2 + k^2 + l^2}}$$

where h, k, l = the usual values
m = numbers indicating extension of the particles in the given direction

Thus even in a cubic crystal the shape of the particle influences the values of η.

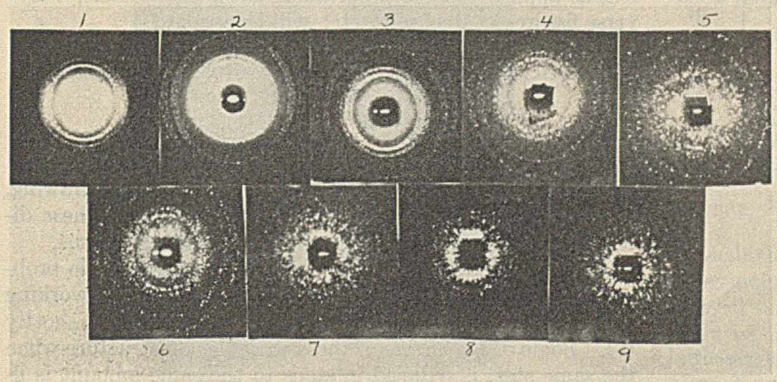


Figure 14. Standard X-Ray Diffraction Patterns for Increasing Grain Size in the Microscopic Range

1. 0.009 mm.
2. 0.012 mm.
3. 0.020 mm.
4. 0.033 mm.
5. 0.037 mm.
6. 0.045 mm.
7. 0.065 mm.
8. 0.085 mm.
9. 0.095 mm.

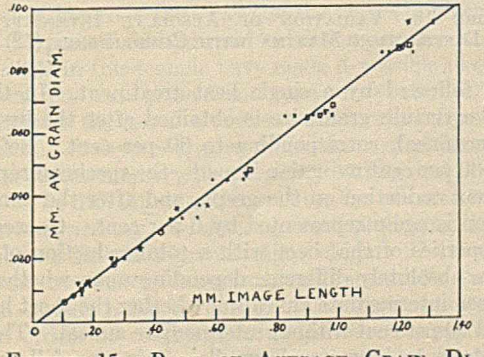


Figure 15. Plot of Average Grain Diameter *vs.* Image Length

Series A, α brass	Series B, α brass	* Series C, α brass
· Small camera	☐ Small camera	○ Steel
× Large camera	△ Large camera	

The technic of particle-size measurement has now been so much improved that there is little doubt of the validity and accuracy of the method. These equations have been carefully tested by Brill, using electrolytic nickel, the particle size of which can be exactly controlled by the sulfur content of the electrolyte. A very detailed analysis and test of the equations has been made by Clark and Zimmer (*8*) on colloidal gold and silver sols from Heyden Fabrik, Dresden, Germany; nuclear gold sols by the method of Rinde; hydrous oxides; alcohol sols of alkaline earth carbonates, etc. In the case of the last substances which were postulated by Buzah to be dimethyl alkaline earth carbonates, identical patterns were obtained as with the carbonates themselves, indicating that these are merely adsorption complexes. A detailed paper will appear later. Figure 11 shows patterns made in the writer's laboratory for hydrous cadmium hydroxide precipitated at 25°, 40°, and 100° C.; the effect of temperature on grain size is easily apparent. Figure 12 shows the pattern of supposed dimethyl barium carbonate compared with pure barium carbonate. Figure 13A is the crystal spectrum from a silver sol with a particle size of 21×10^{-7} cm.; Figures 13B and C are for gold sols with sizes 13×10^{-7} and 2.1×10^{-7}, respectively.

Grain-Size Measurement in the Microscopic Range

Heretofore practically no recourse has been taken to x-ray diffraction patterns for measuring or checking grain sizes in the microscopic range. Certain assumptions are, of course, always involved in microscopic study of size and number of grains per unit area or volume. Utilizing the same samples of brass with which the standard A. S. T. M. photomicrographs were prepared, Clark and Zimmer have found it possible to determine grain size from x-ray diffraction patterns when suitable experimental precautions have been taken. For grain sizes larger than 10^{-3} cm., the patterns illustrated in Figure 14 for cylindrical camera exposures are characterized by spots due to reflections from single grains. A measurement of the length of these spots or flecks leads to a measurement of the grain size. In Figure 15 the microscopically determined grain diameters are plotted against the image lengths of the diffraction interferences. The results prove a satisfactory linear relationship and indicate the excellence of the standard

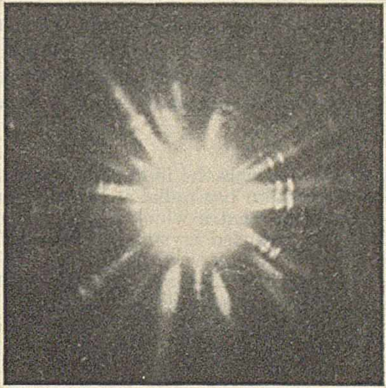


Figure 16. Pattern Showing Radial Streaks Due to Strain

Armco iron reduced from 0.008 to 0.006 inch by hammering microscopic values as well as the validity of the x-ray method. An entirely independent set of brass samples from another source, and various steel specimens fully confirmed that this plot can be used in all cases where there is no residual fiber structure in the metal, and where due attention has been paid to divergence of the x-ray beam and to other variables. The new method should be of particular value in determination of grain sizes of materials with which difficulty is experienced in resolving grain boundaries (which is essential for microscopic evaluation), and in the detection of grain growth during the first stages when none of the grains have been completely absorbed and the grain count remains unchanged.[1]

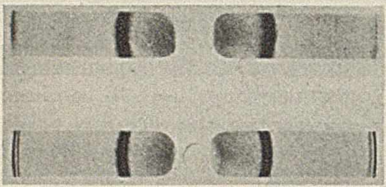


Figure 17. X-Ray Diffraction Pattern Illustrating Strained (Above) and Unstrained Tungsten

Detection and Estimation of Internal Strain in Crystals

One of the greatest of all applications of fine structure analysis by x-rays is in the detection of internal strain or deformation. Polarized light gives very satisfactory indication of this condition in transparent objects, but there has been no satisfactory method for opaque materials. Certainly it is this condition which precedes failure of structure, and it must be eliminated by proper heat treatment. The elimination as indicated by the x-ray pattern is also an important practical consequence leading to proper heat treatment. Only the briefest outline of achievements can be given here. Internal strain is indicated in three or more ways by x-ray patterns:

For large-grained materials the individual sharp spots become elongated, and the pattern has radial streaks (Figure 16).

For small-grained aggregates which give continuous powder-diffraction lines, the distorted crystals produce diffuse and unresolved crystal spectrum lines as contrasted with the sharp lines characteristic of unstrained material. Figure 17 shows such a comparison for unstrained and strained tungsten.

The latest and most quantitative method due to Hengstenberg (*12*) depends on the measurement of changes of intensities for given diffraction lines. For example, the ratios of the intensities of the diffraction lines for the 2,0,0 (second order of reflection from the cube-face planes) to the 4,0,0 lines (fourth order of reflection from the same planes) are as follows:

		I_{200}/I_{400}[a]
Tantalum	Unstrained	5.05
	Strained (cold rolled)	7.0
Tungsten	Unstrained	8.35
	Strained	9.4
	Heated to remove strain	8.5
Molybdenum	Unstrained	4.55
	Strained	6.25
	Strongly strained (hammered)	7.5

[a] I = intensity.

Quantitative measurements of absolute intensities were made on single crystals of potassium chloride with the results outlined in Figure 18 which shows the intensity plotted against percentage of deformation (compression) for the 6,0,0, 8,0,0, and 10,0,0 interferences (sixth, eighth, and tenth orders of reflections from the cube-face planes). These results are in good agreement with theoretically calculated intensity changes. Such results have been fully confirmed by researches in the writer's laboratory.

Besides a mechanical deformation, a crystal lattice can be strained also by the introduction of foreign atoms. These new results represent very considerable advances in this important field of application of x-rays as a tool. Further progress as applied to such problems as fatigue of metals, transverse fissures in steel rails, etc., will be awaited.

Practical Studies of Rolling and Heat-Treating Metals

Many researches have been undertaken in this very important practical field, dealing with the type of preferred orientation produced by cold work, such as rolling, drawing, etc., and the effect of heat treatment in removing these directional properties as indicated by x-ray fiber patterns.

A careful x-ray study over three years of the whole problem of the effect of a large number of variables in working and annealing of commercial metals will be published shortly (*6*). Some of the effects of these variables on structure when the same steel is reduced in steps to the same amount is illustrated in Figure 19 where intense fibering is found for *S*-2 and none for the corresponding *H*-2. Among numerous interesting facts one illustrated in Figure 20 is selected. The expression of results in a three-dimensional diagram of amount of cold work *vs.* temperature of annealing *vs.* some property such as grain size, has been previously employed, but in this work it has been possible to obtain practically complete results with the help of x-ray patterns for measuring one of the important variables. From this graph it is apparent how accurately the whole process may be predicted and controlled. For example, a study is made of a low-carbon sheet steel reduced 90 per cent; in one way, by reducing 30 per cent, annealing, reducing another 30 per cent, annealing, reducing a final 30 per cent and annealing; and in another way by making a 90 per cent reduction without intermediate anneal, followed by a single heat treatment. In the first process a certain grain size is obtained after the first intermediate anneal, corresponding to 30 per cent. Before the second 30 per cent reduction is made, the specimen represents 0 per cent reduction on the graph, and after the anneal the condition is again represented by 0 per cent. Consequently the properties of the sheet with a total reduction of 90 per cent are absolutely different, depending upon whether there have been intermediate anneals or whether the sheet has been reduced 90 per cent without intermediate anneal. The latter would tend to have much smaller grain size following the heat treatment except at the very highest temperatures. If, however, large grains are desired, it is sufficient only to give a light pinch pass which brings the material back to the left

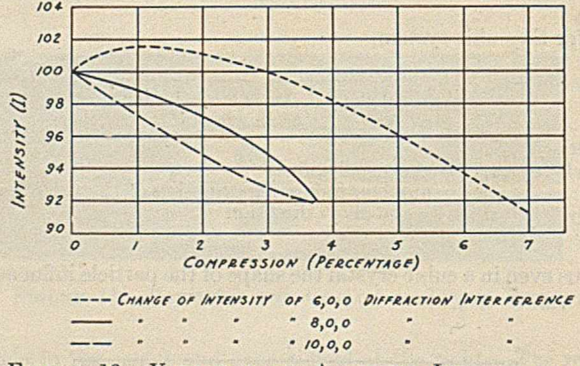


Figure 18. Variation of Absolute Intensity of Diffraction Maxima with Compression (*12*)

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[1] A detailed paper will be published later.

side of the solid figure. The assistance given by x-ray data in working out these rational graphical representations of actual materials has been most gratifying, as has been the verification of scientific predictions of metals of superior qualities for given purposes from such diagrams.

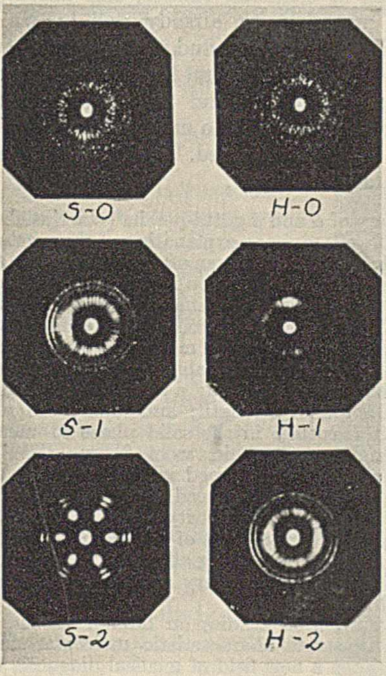

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Figure 19. Comparison of Structures of Sheet Steel Reduced the Same Amounts in Successive Steps on Two Different Types of Cold Mills, *S* and *H*

Marked difference is shown after second step between *S*-2 and *H*-2

New Methods of Studying Molecular Orientations

The fact has been known for several years that long-chained carbon compounds will form thin layers in which the molecules arrange themselves in regular fashion perpendicular, or nearly so, to the plane of the layers. X-ray diffraction from such layers gives a measure from the diffracting spacing of molecular lengths, as well as the direct evidence of molecular orientation. Interesting and important results have been obtained for paraffin hydrocarbons, alcohols, acids, esters, ketones, soaps, etc. One of the most recent studies is that of Clark and Smith on fractionated paraffin wax (7). In most instances the film is placed on a flat backing, and the whole oscillated in an x-ray beam in order that the proper angle of incidence of the x-rays on the planes of given spacing might be passed through and reflection occur. Recent developments in this technic have made it possible to eliminate this cumbrous arrangement and use a curved surface. Figure 21 illustrates the use of a mercury drop, originally suggested by Trillat. A drop of the liquid (solution or molten solid) is touched to the mercury drop, and spreading and orientation occur. The diffraction patterns show the oriented molecular film on the mercury, the mercury itself producing little complication on the photographic film. Figure 22 shows a pattern from the writer's laboratory so prepared for an oil used in high tension cable insulation. The inner sharp rings are several orders of reflection from the film corresponding to molecular length, and the outer strong rings represent the cross-section spacings for these molecules. A very simple and powerful method of examining such substances is thus afforded. Surprising results are obtained in this way for asphalt, linseed oil, wood extract, gelatin, etc., as well as for long molecules. Instead of the mercury drop, a cylindrical curved surface of any metal, glass, quartz, wood, paper, etc., may be used to study the orienting effect of the backing. By such methods as these, the Harkings-Langmuir theory of molecular orientation at interfaces is fully substantiated. In the outer surface or skin of congealed molten drops of salts and even of glass, the fact that molecular orientation has actually taken place is indicated when this reflection method is employed.

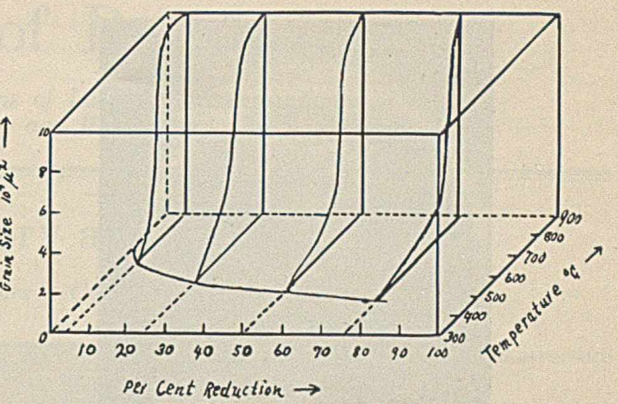


Figure 20. Recrystallization of Cold-Worked Metals

Shape of Molecules

One of the most important contributions which analysis of x-ray diffraction data could be expected to make is information on the shape of molecules, particularly of organic compounds, and the test of theories of molecular structure derived from chemical considerations. With increasing knowledge of interpretation of intensity data, great progress is now being made, particularly following the very convincing proof by Mrs. Lonsdale that the carbon atoms in hexamethyl benzene lie perfectly flat in a single plane. One of the controversies has been as to whether the benzene nucleus was puckered as in diamond or flat as in graphite. The general conclusion was that in naphthalene, anthracene, etc., studied years ago by Sir William Bragg, the ring was puckered while in hexamethyl benzene it was flat. In spite of the fact that the x-ray intensity data are fully in accord with a flat six-sided ring, supposedly very symmetrical, yet the crystal symmetry of hexamethyl benzene is triclinic with a center of symmetry only. The same is now found to be true for benzene, naphthalene, and anthracene, which are plane molecules but possess a much lower crystal symmetry than would be anticipated. Therefore in crystallization, a very slight deformation, insufficient to affect the essential truth of intensity interpretations of flat regular rings, but enough to reduce the

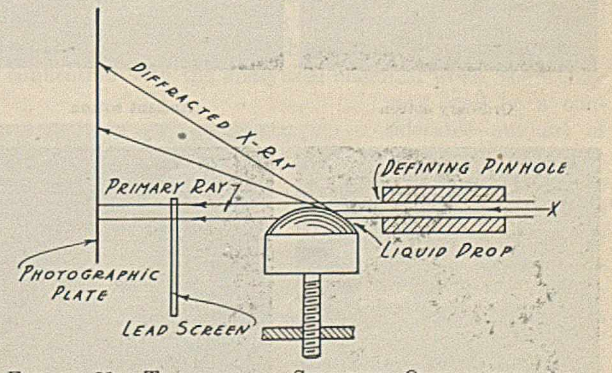


Figure 21. Technic for Studying Orientation of Molecules in Thin Films and at Interfaces

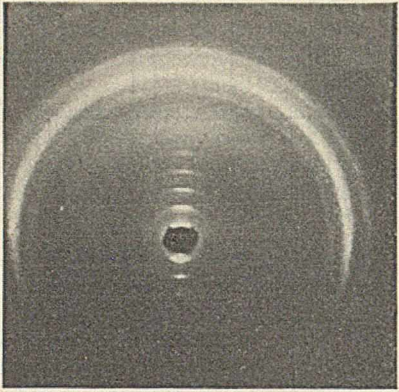
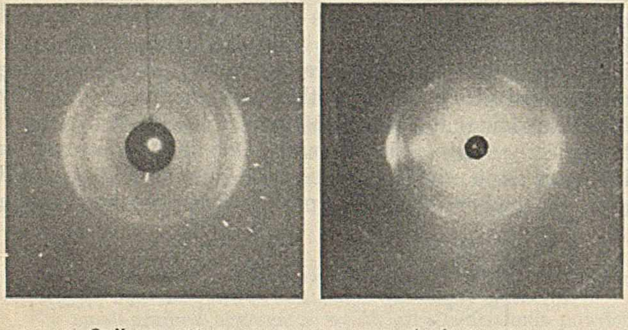
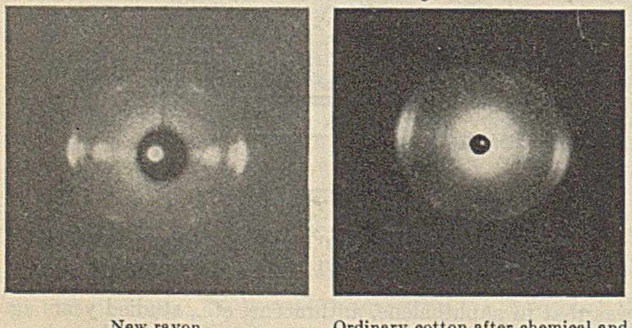


Figure 22. Diffraction Pattern Obtained from Thin Film of Insulating Oil Used in Cables When Oriented on Mercury Drop

crystal symmetry, has occurred; or the hydrogen atoms which are too light to affect intensity data may produce the effect. This explanation clears up the long controversy so that there is little question that the aromatic nucleus is flat while cyclohexane is distinctly puckered. The results have been verified by electron diffraction also (*18*). These x-ray data effectively eliminate the Kekulé static model of the benzene ring with three double bonds, for certainly three of the valences of carbon are co-planar, and the fourth must be disposed to give the ring as a whole a center of symmetry.



Ordinary cotton Ancient cotton



New rayon Ordinary cotton after chemical and mechanical treatment

Figure 23

New measurements of x-ray scattering of gases by Debye and electron diffraction by Wierl prove that in methane derivatives the tetrahedral molecular shape is characteristic only of fully substituted compounds, such as carbon tetrachloride, while in chloroform, etc., the tetrahedral symmetry is lost.

These are only a few of the numerous examples of the application of x-rays in testing of molecular structure. In general, the molecular models (including stereoisomers) of organic chemists have been fully substantiated.

Structures of Polymerized Natural Materials

The achievements of x-ray diffraction science in deducing the structures of cellulose, rubber, silk fibroin, and other polymerized materials are already well known. The long chains of $C_6H_{10}O_5$ in cellulose and of C_5H_8 in rubber, the structure of micelles formed from bundles of these molecular chains or macromolecules, and the arrangement of micelles varying from "brush heap" to nearly perfect preferred orientation, have all been disclosed. A few recent developments only will be tabulated here:

The discovery of α and β gutta-percha (von Susich and Hauser, Clark and Stillwell) gives an explanation of the crystalline portion of gutta-percha, balata, and even of crystals isolated from rubber.

Practical comparisons of cotton in the writer's laboratory (Figure 23) show the pattern for ordinary cotton with long arcs, proving the spiral arrangement of cellulose micelles; one of several ancient cottons from Egyptian mummies, Peru, etc., proving a high degree of fibering and probably superior tensile strength, not observed for any modern cotton; a new rayon with highly fibered structure and superior strength; and finally the result of subjecting ordinary cotton in the solid phase to mechanical tension. By this same technic, wool fibers, silk fibers, catgut sutures, etc., can be strengthened whenever a greater degree of preferred orientation is introduced.

Proof of a remarkable similarity of structure in human hair, porcupine quills, and wool, and of the transformation from α to β wool structure upon stretching about 30 to 40 per cent has been obtained. This work of Astbury and Street has been extended by Clark and Hayden.

Extensive diffraction studies on human tissues, normal and pathological, illustrate characteristic molecular and structural changes, and open a new field of medical diagnosis (*4*).

The essential structural similarity of stretched natural rubber and of synthetic polymerized chloroprene, the first artificial rubber to produce a typical crystal fiber pattern (*3*), has been proved.

A "melting curve" for rubber has been determined solely by x-ray patterns; the percentage elongation of the stretched sample is plotted against the temperatures at which the crystal fiber pattern just disappears. This temperature increases with increasing elongation. Above the area so plotted the rubber is always amorphous and below it is crystalline (*17*).

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Management of Research

A Series of Articles Considering the Functions of Laboratory Organization and the Coördination of Laboratory and Plant Effort

Coördination of Laboratory and Plant Effort

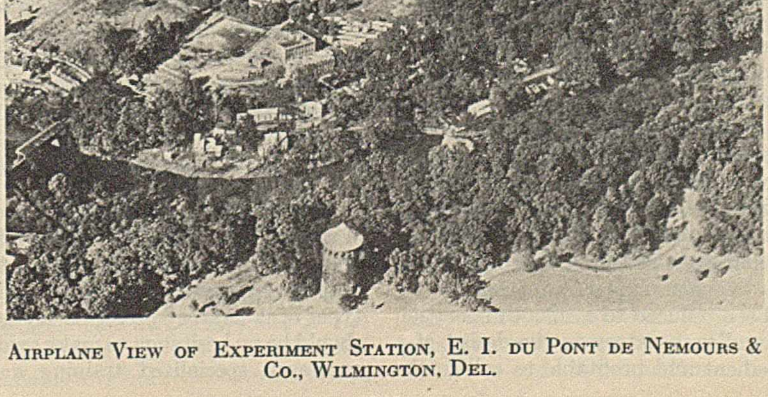
C. M. A. Stine, *E. I. du Pont de Nemours & Company, Wilmington, Del.*

THE larger research laboratory employing, as it always does, a wide variety of technically trained employees and of skilled labor, involves all the administrative questions which are legitimately part of the operation of a manufacturing plant, together with, and in addition to, many special problems of management involved in the harmonious and coördinated effort of a corps of diversified highly-trained specialists. There are, to mention a few examples, such problems as the provision of adequate laboratory facilities and a corps of specialists in the trades, and probably, of an intelligence division to assist in the investigation of the technical and patent literature, in the abstracting and cross-indexing of the progress, monthly, and final reports of the research organization itself, and, in general, the provision of the necessary facilities for making immediately available the accumulated results of scientific work. It is obvious that the proper handling of a large research laboratory will, therefore, call for a high order of executive ability which is advantageously coupled with a thorough training in the methods of scientific research.

C. M. A. Stine

Functions and Responsibilities of a Research Laboratory

A laboratory for the conduct of research along chemical lines has a number of closely related functions and responsibilities. The fundamental responsibility of the research laboratory is the development of new processes and products, and the investigation and development of new reactions, together with the study of the physical and chemical properties of industrial products, with a view to an understanding of the fundamental structure of these products in order that their properties may be correlated and related to their structure and composition.



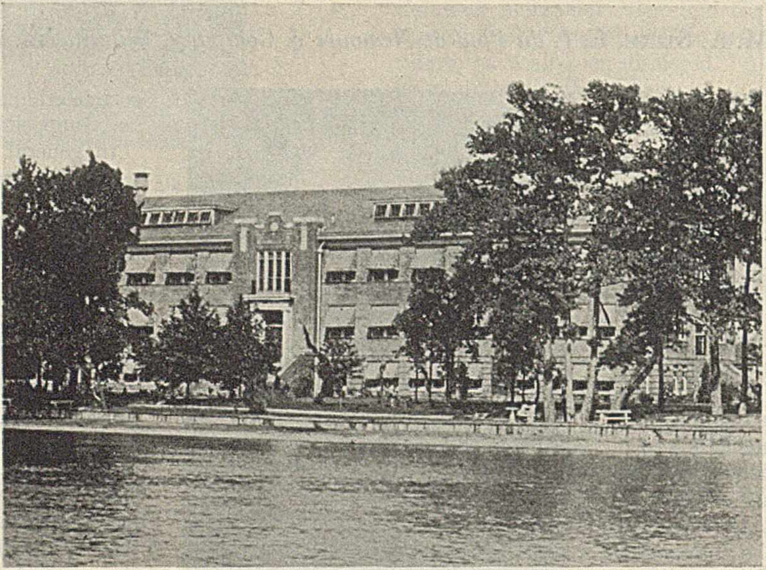
Airplane View of Experiment Station, E. I. du Pont de Nemours & Co., Wilmington, Del.

In general, the work of such a research laboratory may be classified as fundamental research and applied research. It will almost certainly develop in time that there is a necessity for a limited amount of fundamental research work in pure science. This condition, when it arises, should be recognized, and suitable equipment and personnel, together with proper working conditions, provided to facilitate this type of work. With only this passing mention of the very important subject of fundamental research in the industrial laboratory, let us turn to a consideration of the applied research. In connection with the applied research there are control analyses and analytical research, the laboratory development, the semiworks and pilot-plant studies, and the literature and patents investigations.

Connected with the analytical research work, as well as with the semiworks or pilot-plant activities of the laboratory, is the very important work involved in the development of suitable reactions for works control, in order that manufacturing operations may be intelligently followed, stepwise, in the plant, and the diagnosis of process difficulties rendered easier because of methods for the localization of the difficulty. In connection with the analytical chemical work, there may very well be a considerable amount of work upon check analyses, which serve as umpire samples to standardize the methods and results of the various analytical laboratories of a company. However, it is clearly recognized that most of the routine analytical work of a company is performed outside of the research laboratory in suitably located laboratories which are designed for the purpose they serve. There is, in addition to this type of analytical work, a certain amount of research work looking to the development of new methods of analysis and to the development of methods for the analysis of new products produced in the research laboratory.

Necessity of Coöperation between Chemist and Engineer

When a new product or process is still in the test-tube stage, it is profitable for the research chemist to have a certain amount of contact with the chemical engineers who will subsequently assist in the design and operation of the pilot plant, in order that the process may be studied upon a semiworks scale. This contact should be with a view to developing practical questions involved in the subsequent manufacturing operations contemplated, such as the selection of materials of construction, design and arrangement of apparatus, simplicity of plant, and ease of control. It is frequently possible to modify steps, or there may even be an alternative choice of complete reactions for the research chemist engaged in the development of a product or process, so that it is well for the chemical engineer, as well as for the research chemist, to consider the process in the early stages of development.



Technical Laboratory at Dye Works of E. I. du Pont de Nemours & Co., Wilmington, Del.

In the case of the chemical developments of larger companies, it has frequently been found profitable to erect a type of semiworks building very similar to the chemical-engineering facilities provided for the study of unit processes in some of the better-equipped technical schools and universities. These buildings consist of a somewhat tentlike structure of structural steel within which the apparatus is set up with a view to the development of various processes of manufacture, involving the shifting of equipment from place to place and the interchanging of various types of operations and equipment from time to time. This involves the support of the various units of equipment from the floor, rather than hanging the equipment upon the walls of the building.

It has frequently been found expedient to have a well-trained and experienced chemical engineer in charge of chemical operations of this type. He will provide himself with chemists and engineers suitable for carrying on various types of semiworks operations and will, in time, accumulate a wide range of experience quite invaluable in the reduction to practice of new processes.

This type of semiworks organization can, with much profit, assist the research chemist in the early stages of the development of a new product or process. If the research chemist accompanies his process into the semiworks development, as is almost invariably the case, much time and money are saved by having available an experienced crew of semiworks operators.

When the process has been reduced to a smooth operation upon a semiworks scale, and preparatory to the design of a full-scale plant, it is expedient and profitable to call in the man, or men, who will subsequently be responsible for the successful conduct of the manufacturing operations, familiarize this skeleton production crew with the operation, and then turn over the operation of the semiworks plant to this skeleton production crew for a period of time. When the full-scale plant is subsequently ready to operate, the starting and smooth operation of this plant is greatly facilitated by following the above course in the development of the semiworks process.

Importance of Co-operation of Well-Trained Physicists

In connection with the technical research of a large chemical-research laboratory, it is invariably profitable to associate with the research chemists and chemical engineers some well-trained physicists. These physicists are men who have carried on physical research and have doctor's degrees in physics. It is also interesting to mention in this connection, while speaking of the various types of special personnel which have proven their value in a large chemical-research laboratory, that, if the laboratory is fortunate enough to pick up a chemical engineer or physicist with a special genius for mathematics, there is plenty of opportunity for him to exercise his penchant for mathematical investigations.

Importance of Investigation of New Tools

Experience has shown that it is quite indispensable for a chemical-research laboratory, of the type under discussion, to investigate any new tools which pure science may have developed for the study of the constitution and properties of matter. In connection with the investigation of the physical properties of finished materials, the actual structure of the more or less complex materials is unavoidably a matter of basic interest in an effort to correlate properties with structure and composition. An investigation of this type will, therefore, involve the use of such tools as the x-ray, perhaps the ultracentrifuge, and other types of physical apparatus for the study and determination of such properties as hardness, flexibility, distensibility, tensile strength, covering power, hiding power, drying, wetting, and solubilities; the compositions of matter known as colloid, solid and liquid solutions, and dispersion; and the various operations of solidification, polymerization, sublimation, crystallization, etc.

Importance of Employment of Specialists

This, of course, leads to the necessity for the employment of specialists. If the work of the laboratory is not of sufficient volume to justify the purchase of the full time of specialists, at least the necessity for the attention of a specialist to certain types of laboratory problems should be recognized, and there should be no hesitancy to make available to the laboratory the necessary specialized training and experience. The misconceived desire of younger and inexperienced chemists to be wholly self-sufficient in dealing with problems beyond the range of their experience and training, while it may frequently flow from an entirely laudable desire to know all about a problem, should be properly directed and regulated. It is as pernicious in its results as the attitude of the specialist in the university laboratory who recognizes no interest and no virtue in any type of work save that in his specialty.

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Preparatory Stage of Research

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Before starting research, it is essential to have as complete a picture as possible of what it is desired to accomplish, of the obstacles likely to be encountered, and the likelihood that the results obtained will be worth while. Each research problem must be analyzed and its elements carefully evaluated. In so far as possible the problem must be considered in its relationship to other similar problems in order to know its comparative importance. A too limited view of the problem is often the main contributing cause of failure to obtain anything worth the effort put into the investigation. The preliminary consideration of the problem will vary in accordance with the nature of the work. In certain cases the results of the analysis of the problem will suggest a limited amount of exploratory experimentation to permit the formulation of the research problem and to indicate if further expense is justified for the preparation of the data essential to a decision as to whether or not the research is worth undertaking. In other cases research problems are definite enough to permit a decision, and no preliminary investigation is necessary for the formulation of the plan of attack. In some cases it may not be possible to complete the analysis of the problem until literature, patent, and economic surveys have been made, Generally the expense for such work should not be incurred until an analysis of the problem indicates that the research is worth doing. The preliminary analysis of the problem made, the next step is to secure all the available information that might help in planning the research. The search for data bearing on the problem should be done thoroughly and should include the chemical literature, patents, and trade journals. It should be broad in scope; otherwise much useful information will be missed and considerable unnecessary laboratory investigation conducted. It is not enough to find out that a solution to the specific problem has or has not been published. A satisfactory survey should produce all the information that might help to guide the research to a successful conclusion or might lead to a decision on the plan of attack with greater certainty. After obtaining the available information, it is essential to correlate it and try to understand its significance. Reported failures to secure results do not always mean that the research contemplated should be abandoned. In evaluating the data it is essential to try to see the viewpoint of the previous investigators and to find out, if possible, to what degree the results were limited by the scope of their investigations. All information that is relevant to the problem, whether positive or negative, should be included in the evaluation.

Economic Factors

As early as possible in the preparatory stage of research the economic factors should be considered. In the consideration of the economic side of research, common sense must dictate what course to pursue. It is obvious that research should not be undertaken if the available evidence indicates that the result to be expected will not be worth the cost of the effort to obtain it. In any event, the research director must strive to estimate both the cost of the work contemplated and the value of the results to be expected. In the estimate of the potential value of the research there must be taken into consideration more than the direct earning power of the knowledge to be secured. The results may have no direct application and yet be very valuable. They may add to the fundamental facts essential to a better understanding of what is now being done, or suggest a better way of securing the same results now obtained and thus contribute much to the present earning capacity of the processes in operation. Also, such fundamental knowledge may open up new paths of research that will accelerate progress and benefit humanity. The criterion of value in the ultimate must be the degree to which the research adds to the fulfilment of life. That research is costly, no one can deny. The important question is, does it pay? This is the question that must always confront both the directors and the investigators in research, and together they must see that everything possible is done to minimize the work that does not pay and to learn to choose more and more wisely the investigations that are likely to be worth while.

In seeking to determine if a research is worth while, it must be estimated what effect its successful outcome will have on what we already know and have. If it is likely to add to the sum of knowledge; if it may improve what we now have or create something better than we have to fill an existing need; if it results in the production of new things to fill new demands; if it gives insurance that the efficiencies of the present are all that are to be expected: then the cost is justifiable and ultimately it must pay. This is not only true of industrial research, but also applies to pure research. Of course, the problem is more acute in industrial research, but waste in research is tragic wherever it occurs. There are no infallible means of knowing what research will be successful. The best that can be done is to consider all the factors in each case and then use one's best judgment. The results will be good or bad, depending upon one's range of vision and capacity to understand and interpret the data he has.

In the preparatory stage of industrial research nothing is more important than a market survey to ascertain the needs that exist and how well they are met by the products now available. No desirable end is accomplished by merely substituting a new product for an old one. In fact, much harm might be done and capital endangered or destroyed. To justify itself the new product must possess some advantage: it must be cheaper; or it must give better service in satisfying a demand not adequately fulfilled; or it must create a new demand which will not conflict with existing demands; or it must enhance the service of existing products, making them more efficient than they now are; or it must make possible new processes which will result in increased efficiencies and lower costs of production.

SOURCE OF RAW MATERIALS

In the preparatory stage of research it is also essential to consider the source of raw materials. Many a brilliant concept has gone down to oblivion in industrial research because no adequate source of raw material was available at a price which made the development possible or desirable. The consideration of the raw material must embrace the source, quality, location, and the cost of making it suitable for use, and of transporting it to the point of use. The consideration must also give due weight to the by-products which will result, either in the preparation of the raw material or in the development of the finished product, and estimate the effect these will have on the quality, cost, and utilization of the finished product. The synchronization of manufacturing processes so as to utilize the total production of isomeric products and the creation of a demand for the balanced production constitute problems of grave importance to chemical industry. They are among the most important problems to be considered in the preparatory stage of research.

In planning industrial research, considerable thought must be given to the question of the effect of such research on the general sales picture. What will the contemplated change do to the sales situation? Will improvements in production introduce a sales-resistance factor which will offset the advantages to be secured? If so the advantages must be great enough to justify the cost of overcoming this sales resistance. This problem is particularly complicated when the products are sold on the basis of the effect which they are capable of producing and not on the basis of chemical purity, as is true with dyes.

Good preparation is essential for wise planning, and this is indispensable to successful research.

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Functions of a Laboratory Organization

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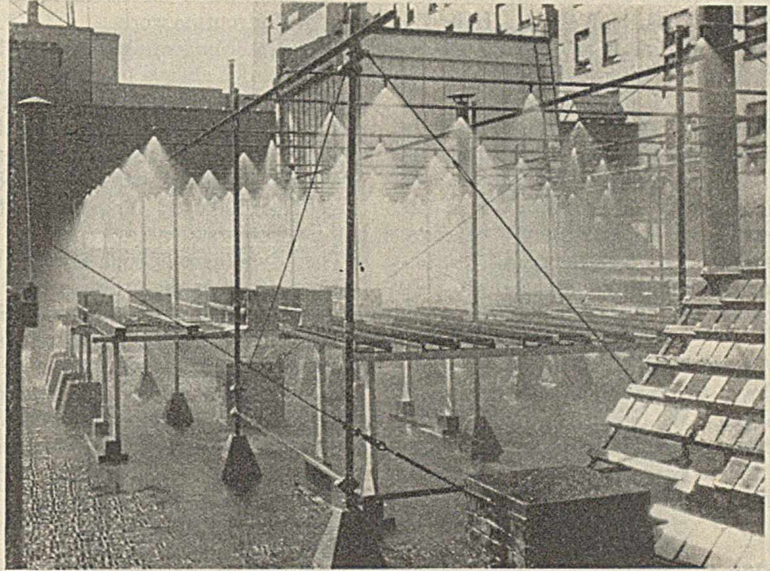
ROBERT R. WILLIAMS

THE purchasing department of an industrial organization complains of the rising cost of a particular raw material and asks its laboratory to develop a substitute. Preliminary investigation reveals that the fundamental requirements underlying the specification under which the material is bought are somewhat vague. No one knows just which properties of the material are essential and which are incidental. The history of the adoption of the material indicates that it was chosen on the basis of a factory trial which merely showed that it worked. A study of the manufacturing process is initiated in conjunction with the manufacturing engineers and of the service conditions by collaboration with the consumer. Research men versed in the fundamentals are consulted who presently come to reject certain prevailing ideas about the material and its use as doubtful or erroneous and to select others as plausible. The latter are explored experimentally and an idea is generated which later becomes a conviction that the important and unique property of this material is at bottom a low-temperature coefficient of baking reaction. This low-temperature coefficient is important because it avoids the necessity for a supposedly difficult temperature control in the manufacturing process. But it is found possible by drawing on laboratory experience to devise an automatic temperature regulator for the factory apparatus. Trial of this regulator not only makes possible the use of a cheaper substitute material, but discloses an unexpected improvement in some quality of the product, supposedly unrelated to the question which provoked the investigation.

So, in the purchasing needs of an industry, begins one laboratory enterprise. Many industries, like the one referred to, consume raw materials which require laboratory evaluation but may produce a commodity which need only be evaluated by the practical test of salability. This tends to be true most often of producers of articles for household and personal or family use, as the retail buyer is guided by general appearance and reputation rather than rigorous and exhaustive test. Tooth brushes and automobiles, domestic refrigerators and clothing are random examples. In a typical case of this sort the purchase and manufacturing use of raw products may jointly determine the nature of laboratory activity.

The chief business of some laboratories is devising new processes, rather than the modification or control of old ones. Numerous instances might be cited in which the entire economics of a commodity have been overturned by the development of a new process for making the material more cheaply. This is perhaps especially true in chemical industry. Notable examples during the past two decades are the cracking processes for production of gasoline, the Weissman fermentation of starch to acetone and butyl alcohol, the synthesis for methanol and probably most memorable of all, the fixation of atmospheric nitrogen. When such radical innovations are involved, the details of purchasing economics sink into insignificance.

Another manufacturer may be producing an article which permits little freedom of choice of raw material or process. Such enterprises are usually highly competitive, yet the producer may often profitably spend substantial sums in the study of the quality of his product and base his sales competition upon quality rather than price. This can best be done in cases in which the market is governed to a great extent by the purchases of large concerns who can afford to and do subject their purchases to a careful laboratory appraisal. In such appraisal the buyer, as well as the more competent producer, is often served by such agencies as the American Society for Testing Materials. However, similar appraisal of articles for the use of the retail buyer is sometimes performed as a public service by governmental or private agencies. The work of the American Medical Association and of Federal Government bureaus in the rating of foods and drugs, and of certain magazines in evaluating household appliances and the like, are instances in which laboratory evaluations may be highly important, even for the retail market. On the whole, the heavier role of the laboratory in quality marketing is probably the most noteworthy development in laboratory service during the post-war period in the United States.



Intermittent Artificial Rain to Accelerate Corrosion of Test Specimens

Many examples can be cited in which great laboratory emphasis is placed upon the utilization of by-products or the finding of new or extended uses for old materials. The petroleum industry, for example, has successfully offered by-products in the form of insulating waxes, medicinal oils, insecticides, and volatile solvents. In some of these instances a producer conducts a laboratory ostensibly from the consumer's viewpoint and strives to put himself in the position of consultant to his prospective purchasers. This is especially true of the laboratories of endowed industrial-research organizations and of trade associations, but is by no means confined to them. For example, the rubber and paint industries are furnished with a certain amount of information about pigments by the producers of the pigments; the steel producers are instructed in the virtues of nickel as an alloying agent by the nickel producers; the insulated-wire manufacturers are told by asphalt producers about weatherproofing compounds; construction engineers are offered information about brick, tile, or concrete by those interested in the sale of these products. Sometimes this information consists of propaganda of doubtful virtue, but much of it is honest and discriminating.

In view of the complexity of industry it is to be expected that the laboratory will sometimes function principally as an adjunct to either the purchasing department, the manufacturing plant, or the sales department, as the particular case may seem to warrant. To be of permanent service to any of these departments, however, it must be dominated by none of them; otherwise it lacks judicial character and loses public respect. The truth must always be faced, however unwelcome it may be. It is difficult enough to maintain a disinterested attitude in scientific experiment, because of the natural enthusiasm of individuals. To avoid adding any unnecessary tendency to intellectual dishonesty, the head of the laboratory organization, even though it is small, should be coördinate in authority with the directors of purchase, sales, and manufacture.

Necessity of Broad Industrial Research

A close analysis will often show that over a long view many industries are putting an excessive stress upon that phase of their business which seems to offer the most immediate prospect of profit and neglecting others which might prove of revolutionary importance. Such industries will do well to consider whether their laboratory activity should not be broadened to cover the fundamentals of raw materials, processes, by-products, and the uses and quality of the finished article, even though the primary interest may be in only one of these phases. This course has several marked merits. It greatly diversifies the opportunity for important and eventually profitable laboratory discoveries by increasing the breadth of the experimenter's view. It may lead to an unsuspected source of raw material or to the recognition of a slumbering potential demand. It is in the border lands between the strict fields of the several industries that such unsuspected opportunities are most likely to lie.

A parallel can be found in university life, where there has been a reaction against the departmentalization of knowledge along the traditional boundaries set up for administrative purposes between the departments of our schools. Observation discloses that much of the most fruitful scientific work of the past decade or more has been the result of combining the knowledge and viewpoint of two distinct fields. Examples can also be found of unusual performance by individuals in fields foreign to their primary training. It should not be surprising that ignorance of the details of a subject is often an asset, in that, unfettered by the prejudices of the experts, it leads through independent study to a fresh viewpoint.

Industrial research should therefore be as broad as economics will permit. It should also include a proportion of pure research or, at any rate, research with indeterminate objectives in the commercial sense. Otherwise it will be difficult to acquire or retain men whose interests are primarily intellectual rather than commercial. Such interests are not more or less characteristic of scientists than financiers, for example, except as the work of the scientist requires a familiarity with abstract things often seemingly far removed from workaday affairs. Both scientists and financiers of first rank are characterized by great imagination and desire for creative action rather than by mere money motives.

Scope and Nature of Laboratory Field

The scope and nature of the laboratory's field will be determined primarily by the character of the industry with which it is associated. Its scope and its method will also inevitably be determined in a great measure by the personalities of its leaders. A man of highly imaginative type will often effect an organization which may lack something as to the integration of its activities and systematic coverage of its field but will offset this with the originality of its scattered contributions. A more methodical man may produce an equally effective organization, which will capitalize more fully whatever ideas it develops by its thoroughgoing search. Occasionally brilliance and thoroughness are combined in a single individual, a rare good fortune that industry can scarcely expect in a succession of laboratory leaders, though it will do well to make exhaustive search for such men.

When leaders are changed, especially after a long incumbency, there is often a disconcerting period of disorganization if the personalities involved are of radically different type. The best protection against this is to maintain a large measure of autonomy in the several subordinate groups which compose the laboratory organization. This gives opportunity for the laboratory to become the expression of several personalities rather than of a single one, diversifies the outlook, and stabilizes the organization by a democracy of effort. Indeed a large measure of freedom of method must be allowed to juniors, for creative work is after all largely a product of individual thinking.

The function of a laboratory organization is to secure a broad, well-ordered, and self-extending knowledge of the art with which it is concerned and to make this knowledge available for translation into superior industrial performance. Its function is partly invention but is, even more, education. The student body is primarily the laboratory staff; secondarily, by a sort of extension work, the educational program reaches first the technologists and later the laymen of the industry.

Some of the laboratory's tasks will be those of immediate application; others will have to do with more distant and often unforeseeable changes. We may for convenience designate these two functions as engineering and research, though either word may fail to connote precisely what the writer intends. The desired distinction is one of the immediacy of application.

ENGINEERING AND RESEARCH

Used in this sense, engineering and research comprise the work of any laboratory. There is much to be said in favor of combining these functions in each of the several units of organization. Research stimulates the imagination of the engineer and insures the incorporation in his work of unconventional ideas if they happen to be readily applicable. It spurs him to inquire about fundamental objectives and to examine his projects more critically. Engineering has an equally salutary influence upon research by requiring the experimenter to secure a wider and more practical knowledge of his problem. A research man who has to do some engineering is, on that account, much less likely to offer a solution which is based upon excessively simplified assumptions or to offend his more purely engineer-minded colleague by a know-it-all attitude.

The principal difficulty with such an assignment of work is the same one which the universities have found in combining the functions of teaching and research, or, worse still, the combination of a consulting practice with an educational connection. It is the old difficulty of serving two masters. The inclinations of the man will lead him to neglect one phase of the matter or the other, unless there is consistent effort to secure recognition of the usefulness of the principle of combining the two functions. In any actual case it may be found impossible to make certain men do first-class research or others do first-class engineering. But in the great majority of cases it will be found that the effort to do some of that type of work to which he is less inclined will tend to broaden the man and stimulate him to better work in the field of his preference. Practically it is usually necessary to compromise and allow the individual to spend the major part of his time in that type of work which he likes, but to insist on some consistent effort in the other field.

Administered in this fashion, this principle is of great fructifying value. In almost any laboratory organization one can find sad examples of men, both in research and engineering, who have suffered from neglect of it. Two men starting out may have similar equipment—usually just a fair modicum of brains. One, by reason perhaps of family tradition or college associations, has an ambition to be erudite and goes through life with a sublimated school-boy attitude. The other, for equally accidental reasons, wants to be practical, takes his knowledge out of handbooks, refuses to exercise his brains, and goes to seed in middle life, having missed the most practical things in the world—namely, novel ideas. Certainly we must not accept mere disinclination to humdrum as a qualification for research, or mental lassitude as permissible for routine work.

The idea of intermingling research and a more routine type of work is not always feasible or acceptable to other departments of an industrial concern. The spirit of this arrangement can often be worked out by the simple expedient of inserting in the engineering or development branch of the laboratory a leaven of men with the research attitude and vice versa. The writer believes, however, that the forthright policy is better when practicable.

The advantages of such a policy can well be illustrated by following further the example with which this article opens. That investigation does not end with the installation of the temperature regulator. Research has, in the meantime, begun on the nature of the baking reaction referred to. This reveals that, after all, there are two baking reactions involved, that one of them is advantageous and can well be speeded up with a catalyst, and that the other, which is deleterious, now proceeds at relatively so slow a rate that it can be ignored. This discovery opens up the possibility of use of a number of still cheaper substitute materials, of which one is chosen.

It then occurs to some one that the rate of aging of the material during the service life of the finished article is probably related to the rate of baking in the manufacturing process. Accordingly the selection of a material for the purpose is reëxamined in the light of data on aging which are accumulated by an extended study, including the theory of organic oxidations. Ultimately a material is found which is not only cheaper but more durable than the original. In addition the manufacturing process is speeded up and costs are thereby reduced. The quality of the original product has also been improved in several other respects by better factory control and choice of material. Incidentally, the temperature regulator is found well adapted to another manufacturing process.

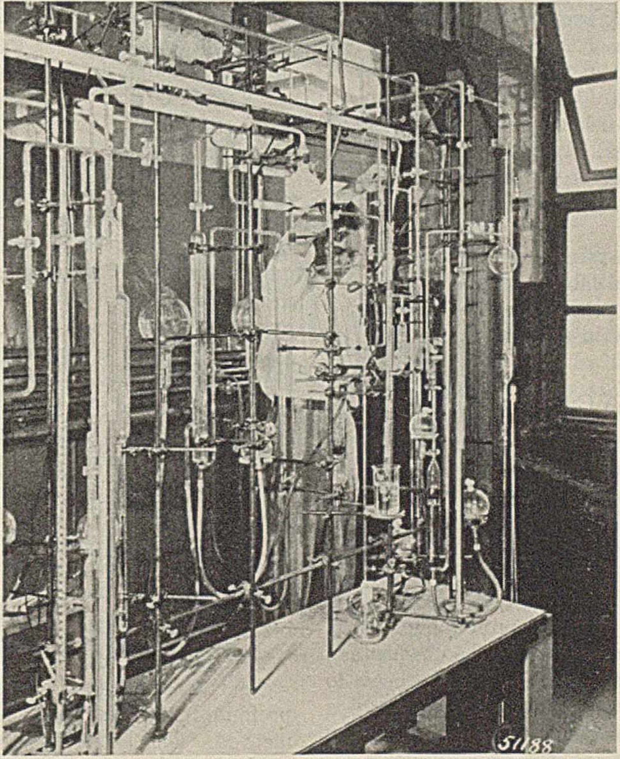
Even when this account is lengthened to include several disheartening incidents encountered by the way, the picture it presents is rosy. But it is no more rosy than is justifiable. The process of completely revamping the original practice may take years, but betterments of the sort indicated are almost inevitable if each major engineering problem which arises is made the basis (or if necessary, the excuse) for the initiation of a suitable research program. In the end one can scarcely say where the engineering left off and the research began.

A particular virtue of this method of procedure is that, in the course of the series of studies, a number of men involved have acquired a thorough and critical mastery of an entire art which was once merely a dull routine manufacturing process. Such a thorough mastery develops a quality of intellectual growth in the group of men concerned. The impulse to apply the principles of that art to allied fields becomes irrepressible by any means short of curtailment of funds.

The writer therefore regards it as fundamentally important to the function of a laboratory that each major line of engineering or development work be supported by a program of research along kindred avenues. As far as possible one should not allow the question "What shall we do?" to arise without raising the questions, "What are the principles involved?"

and "Why and how will the proposed remedy function?" Often there are so many obvious questions about the principles or mechanisms involved that one cannot get funds to pursue them all. Nevertheless, let the research program begin somewhere, preferably on those questions which appear most fundamental or have most excited the curiosity of the available personnel.

It has been our experience in several fields that a research program designed to answer fundamental questions presently results in the accumulation of knowledge which furnishes offhand the answer to numerous other engineering problems as they subsequently arise. All that is then necessary is a confirmatory trial of the idea so supplied. A large amount of expensive exploratory engineering experimentation can thus eventually be eliminated. The resulting engineering economies alone will usually prove sufficient to justify the expense of the entire research program, quite aside from the ideas of a more revolutionary character which grow out of research and which are ordinarily considered its main objectives.



Reactions of Cellulose in Liquid Ammonia Solutions

Publication of Useful Scientific Work

It is now generally recognized that, from the standpoint of dividends to stockholders, it is good business to make corporate policy square with social evolution. In other words, a corporation must justify its existence by rendering a service to society commensurate with the market and legal protection which society affords it. This debt to society can be paid in part by the advancement of knowledge through experimental work of a sort suitable for publication and useful to civilization at large.

A certain amount of such publication is essential to the acquisition and maintenance of well-qualified personnel. Modern life herds men so much into complicated corporate organizations that individuality is too often lost. Publication affords a means of tangible expression of individuality that is greatly valued by men of high motive, such as make up the bulk of our scientifically trained population. It is a just tribute to these men to point out that a desire to render a distinctive personal service to their day and generation is a common aspiration among them.

Today when popular opinion gives so generous a part of its thought and interest to scientific and technical advance, there can be no better commendation of the wares of a corporation than to establish a reputation for high-grade scientific achievement. Unfortunately pseudo-science masquerades all too successfully in the advertising pages of our popular magazines and in radio programs. But there is a large element of our population which wields an influence out of proportion to its numbers, whose good will is acquired only by the more worthy sort of scientific effort. The advertising value of a laboratory of this description, though incidental, is by no means negligible. It must, however, result from a consistent and long-continued effort, not from a fair-weather fancy. Research values cannot be improvised to fit a business boom.

Transfer of Laboratory Results to Field or Factory

A moot question in laboratory management is concerned with the transfer of laboratory results to the field or factory. How far should the laboratory go with a project before subjecting it to commercial trial? While the answer to this question will depend on the nature of the project, the whole matter resolves itself into one of economics. The first primitive determination of the ash of tobacco was made by igniting a ton of the leaves and scraping the ashes together in a box to be weighed on a steelyard. But experimental science began seriously only when men learned to operate on a small scale for the purpose of gaining knowledge. Our pioneer forefathers learned which crops were adapted to their soil and climate by sowing whole fields and proceeding thereafter on the basis of the favorable or unfavorable experience. The scientific method is to plant a few rows or a few square yards of each of the possible crops and acquire some information about them all in a single season.

All experiment, as distinguished from commercial trial, must be justified on similar grounds. Scores, often hundreds, of laboratory experiments can be performed for the cost of a single commercial trial, and the latter should be deferred till the small-scale method has been exhausted. This seems trite, but we see industrial enterprises go on the rocks every year from neglect of this principle.

Aside from low cost, the small-scale experiment is justified by the fact that all factors can be more readily brought within control under laboratory conditions. In order to experiment successfully, only one factor should be varied at a time. This also seems trite, but is often ignored. Often, even under laboratory conditions and with the most careful planning, some uncontrolled factor slips in to destroy the value of the experiment. Commercial-scale operations are far more liable to this error. Our backward industries are those which have confined themselves to the large-scale commercial trial. Accordingly, their technical information is a melange of fact and fancy; their technologists are the most positive in their beliefs.

Many a laboratory has been discredited, however, by failure to appreciate that enlargement of the size of operation usually introduces some new factors. In chemical and metallurgical operations it is the factor of radiation of heat as affected by changed relations of surface to volume that most often wrecks the first large-scale trial. Therefore, unless the proposed project is one which, on the commercial scale, involves only the multiplication of small units, it is nearly always wise to pass through a semicommercial-scale stage. Such experiments are likely to cost several times more than each of the many laboratory experiments which have preceded it, but only a fraction as much as a full-scale operation.

Many industrial concerns, especially in the chemical and metallurgical fields, have adopted such semiworks operations as a part of the regular routine for introducing a new process. In several instances a separate organization has been set up and supplied with flexible miniature factories, especially for such purpose. Ideally we think semiworks operations are best carried out by collaboration of the laboratory scientists and the engineers who are destined to make ultimate commercial use of the development. This facilitates transfer of information from laboratory to field or factory and broadens the outlook of both groups of men. Which group should be in responsible charge of this stage of work should be determined largely by the extent to which the semiworks scale approaches the commercial.

There are two branches of industrial laboratory work which are often neglected. In chemical laboratories the analytical department is frequently a stepchild; in physical testing laboratories there is sometimes insufficient application of theory.

Analytical Department of a Chemical Laboratory

When chemistry was young, analysis was a phase of the subject regarded worthy of the intellects of the masters. Later, useful applications of constructive chemistry involving new processes so captivated the minds of chemists that analysis fell into disrepute. Synthetic organic chemistry was perhaps primarily responsible. In recent years, however, there has happily been a revival of interest in analytical chemistry, in which biochemistry has had a profound influence. Living things are so hopelessly complex that the chemist can only try to analyze them and leave most of the syntheses to future generations. The determination of hydrogen-ion concentration is a case in which biochemistry has furnished an analytical motive. How important this development has been to all chemistry, both pure and applied, can be seen by the most casual reference to current chemical literature.

Another important reason for the disrepute of analytical chemistry is the fact that the analyst is often shorn of all authority and dignity. He is asked to perform endless analyses by a prescribed routine and is permitted no more opportunity for original thought than a typist. Sometimes he takes orders from a man who is himself untrained in chemistry. Not many years ago college graduates in chemistry were carefully warned by their professors to avoid analytical jobs, and it is to be feared that the practice has not yet been outgrown entirely, as it is often difficult to get college men to take an analytical assignment cheerfully.

A possible solution of this problem is to scatter the analytical work among the men who are, for the greater part of their time, engaged in research, but reasons of economy as well as the need for special training in analytical technic argue against this plan. We have found it more advantageous to meet the situation by conferring upon the analyst the right of participation in the decision as to what samples shall be analyzed, how, and to what extent. In short, the analyst becomes a consultant who advises how analysis can be applied to the solution of the problem which lies behind the whole undertaking. In addition, the analytical department is supplied with funds to conduct a supporting program of research in analytical methods and allied theory.

Under this arrangement the usefulness of our own analytical laboratory has grown very greatly (*1*). This experience has been convincing that many problems of industrial as well as pure chemistry which seem formidable are greatly clarified at the outset by development of analytical modes of attack. Many conventionally impossible analyses are performed without much difficulty, if talent of research type is applied. Microchemical and electrometric methods are proving especially valuable.

A critical survey of the schedules of an analytical laboratory will also usually reveal that a great number of needless analyses are being made. Often a more intelligent sampling method, with a consideration of the inherent tendencies to variance of the materials and an elementary application of statistical methods, will justify a substantial reduction in the volume of such work. A survey of this sort requires men of some independence and originality of thought.

Physical Testing Laboratories

Physical testing laboratories are likewise prone to become sterile under a dull routine. A corrective remedy of the type suggested for analytical laboratories is also applicable in this case. The emphasis of modern physics on the structure of matter and the nature of radiation has diminished the available number of research physicists with an interest in the classical branches. A recent editorial in the *American Mercury* amusingly tells of a correspondent's search for a modern book on elasticity, which resulted in nothing more recent than one published in 1885. Many physical chemists are more thoroughly versed than physicists in molecular physics and heat, and often will take a keen interest in such studies as are closely correlated with physical testing, especially of fluids and plastics. Our engineering schools also furnish a considerable number of men with a research background in theoretical mechanics. From these various sources adequate staff can be readily recruited to carry on a revivifying program of research.

Conclusion

Nearly all phases of modern human activity have been profoundly affected by the philosophy of the laboratory method. One hears daily of attempted applications of this method to education, to art, and to the social sciences. That they are not more successful is due presumably to the inherent impossibility of bringing all factors under control wherever the inheritance and particularly the psychology of the experimenter or experimental material is involved. Yet the success of the experimental method in biology and medicine has been extensive and gratifying and promises ultimate progress in still more difficult fields. The laboratory man may therefore justly rejoice in the resources at his command in the field of physical science, and while preserving a due respect and humility in the face of the difficulties of the less exact sciences, have confidence that he is playing a worthy part in the solution of the age-long problems of mankind. Such things as business depressions and technological unemployment are to him but passing phases of progress.

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Direction of Investigation in the Experimental Stage

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H. L. Trumbull

RESEARCH is the systematic exploration of the unknown by trained investigators who are skilled in the application of scientific methods, and require more than the mere ability to reason logically from cause to effect. Their mental equipment should embrace a wholesome curiosity, skill in experimentation, and a directed zeal in the planning and elaboration of experimental work. Above all they should have creative instinct, which is the driving force underlying research. Since the main function of research is to create, to bring into the realm of the known that which previously has been unknown, the originality of the investigator is the first requisite of success in any research enterprise, whether the investigation is being conducted in an altruistic spirit, or in an organized industry where profit from the undertaking may be the activating motive.

Success in conducting a given investigation requires of the research man more than the ability to conceive brilliant ideas. In fact, mere brilliance of conception is not an unmixed blessing, since under its hypnotic influence the skepticism which underlies all critical effort may suffer paralysis. The ability to conduct research combines an intuitive sense and a perfection in experimental skill by virtue of which results are produced which are dependable and verifiable. The investigator must be trained by experiment to discover truth in a form capable of verification by others. It is only in this form that the results of scientific investigations have permanent value as contributions to our knowledge of science.

Progress toward a definite research objective is usually a stepwise, methodical, and cumulative procedure. A logical program of attack on the problem is formulated so that the plan permits verification by experiment at every step. The plan of attack is vital to the success of the undertaking, and should be logical, comprehensive, and critical. An orderly sequence of experiments is frequently imperative, although in some cases intuition may play a major role. After the results of many experiments are available to the investigator, it is often necessary to redraft the original plan of attack in order to modify its scope, to verify some discovery, to change the type of experiment, or to control some variable not recognized as pertinent in the original program. Utilization of the published literature, deep study, and reflection must accompany experimental effort in research. Ingenuity in the devising of apparatus and methods of testing, and skill in technic are continually in demand in the experimental stage of investigations. No form of human effort is more highly individualistic, or more exacting in its demands upon the vitality of the worker, than research.

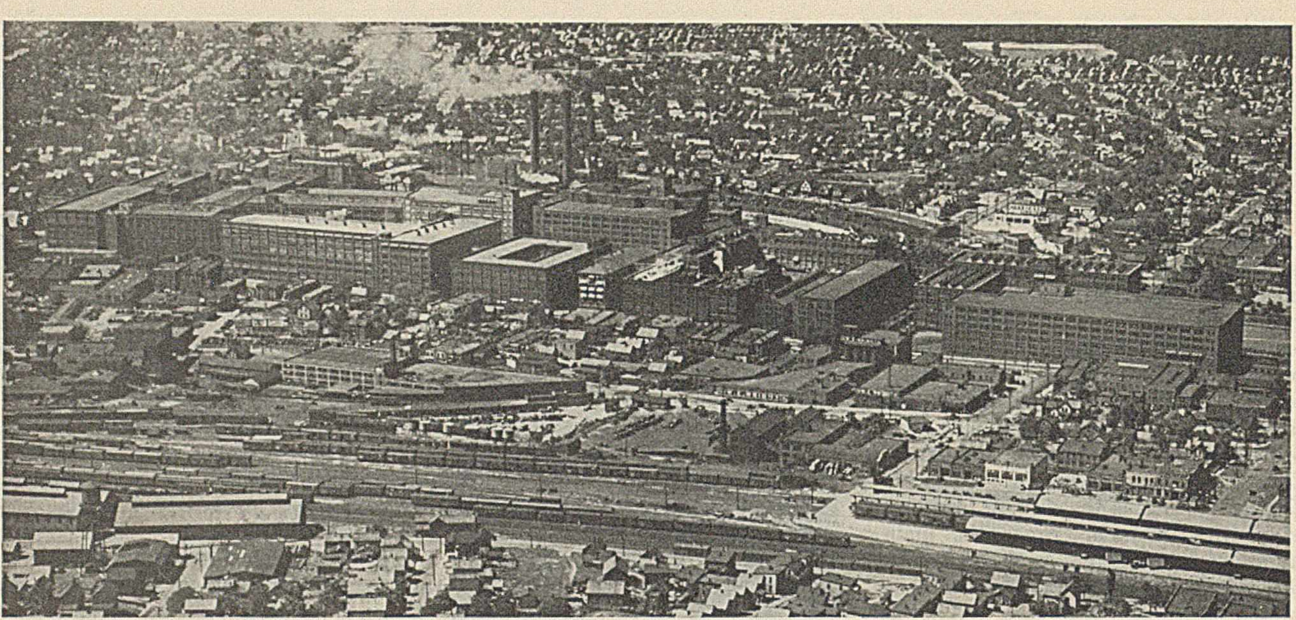
Functions of Research in Industry

Keeping in mind the technic of research, in general, what are the functions and peculiarities of the organization of research in industry? The ideal research laboratory in industry is one which requires the minimum of direction. It consists of a group of congenial scientists working out their ideas in a well-equipped laboratory with as little distraction as possible from the other departments of the industry. If the laboratory staff comprises skilled technicians with maturity of judgment, chosen because of their zeal for research, very little direction will be required. Granted the necessary financial support, such a group of scientists can, without formal organization, accomplish creative work of great value. Why then is it necessary to set up an organization for the direction of research in industry?

In the inception of an industrial-research enterprise, a corporation is faced with the necessity of adopting a program which the officers can approve in conformity with sound business policy. Thus research organizations are, in many instances, required to justify their existence within a period of three to five years. Such a limitation of the research program puts the investigators under restraints which may seriously hamper their productivity.

Among those who are experienced in research it is pretty generally recognized that not only large financial benefits to the supporting company but also advances in scientific knowledge and contributions of direct benefit to humanity usually result from its performance. In recognition of the remarkable fertility of the mind of a productive scientist, wise provision should be made in the research program for the encouragement of contributions to fundamental scientific knowledge and the publication of the results of such studies. Such a policy stimulates output on the part of the active research worker, since the opportunity to be scientifically productive and the publication of the results of investigations are privileges zealously sought by research men. Interest shown by the investigator in fundamental research should be fostered as a vital essential to success in any research program rather than be regarded as foreign to the immediate field of the supporting company's enterprise.

In order to define the function of supervision in the experimental stage of research, it is necessary to recognize the limitations imposed upon research objectives by the company which sponsors the undertaking. Even with a sympathetic and broad-minded sponsorship it is necessary to have a definite understanding concerning the scope of the research enterprise. Unfortunately many such limitations are effected by compromise or neglect rather than by design. The scope of the research program can best be defined by a research director in close coöperation with the responsible directing head of the corporation. Certainly no man who is not a scientist can intelligently formulate the objectives which depend for their elaboration upon the creative efforts of research men. Just as certainly, a responsible business head is needed to determine what measure of financial support the corporation can afford to give to these objectives. To the corporation



Main Plant of B. F. Goodrich Co., Akron, Ohio

an investment of this sort is fruitful in proportion to the wisdom and patience of the executive, and to the clearness of vision of the research director.

Of necessity the scope of the field will have definite limitations. These limitations will depend upon the nature of the industry, whether monopolistic or highly competitive in character; upon the needs of the industry for improved quality, lower production costs, sales appeal, and better service to the customer; and upon other considerations, such as the financial standing of the particular company.

The necessity of continuing the support of research once it has been seriously undertaken by any unit of the industry deserves emphasis. The objectives sought in industrial research are constantly changing in order to set the pace, as well as to keep the pace of the industry. An alteration in the immediate objectives of research is a matter requiring the best available information and good judgment on the part of the research director. Such changes in the program as are concerned with progress can be effected without hampering productivity, if the fabric of the research enterprise carries continuous threads of fundamental scientific studies, which remain unbroken and thus serve to support the whole undertaking.

Problems which are fundamental in character are productive of results which are more far-reaching than the briefer studies included in the research program for their promise of immediate benefit to the industry. Basic problems are time-consuming and require the steadfast support of the management in the face of grave disappointments. The early abandonment of fundamentals retards accomplishment and alienates the confidence of the scientist in the sincerity of his employer, since financial as well as mental stamina are needed to insure the harvest of the fruits of research.

Value of Fundamental Study

An example of the practical value which may result from a fundamental study is the discovery of non-accelerating antioxidants which have effected a marked improvement in the life of rubber products. It has been estimated that this development has been responsible for saving the buying public fifty million dollars annually.[1]

As a preliminary to this discovery many years were spent on the painstaking study of the perishing of rubber. Perishing was found to be caused by oxidation which could be accelerated by heating rubber in the presence of oxygen. Accelerated tests were perfected to prove the effectiveness of antioxidants in a few days or a few weeks as contrasted with the months and years involved in natural aging. The development of these tests alone required nearly ten years.

Chemical studies were pursued to identify the products of oxidation and to determine the velocities of the reactions. It was hoped by this means to throw light upon the mechanism of the chemical change involved. Although it was found in this study that some chemicals effectively retard the rate of oxidation, those engaged in the investigation were not able immediately to prove the course of the chemical reaction and to derive from it profitable commercial application of the knowledge which was then available. Systematic studies of the chemical constitution of retarders finally led to the discovery of a limited class of materials which enabled the compounder to control the rate of oxidation without interfering with the proper cure of rubber compounds. In this improved form rubber antioxidants became at once very attractive commercially. During the time this long study was in progress, many problems in the rubber industry were considered more urgent than the study of oxidation retarders. It is doubtful if any of these more urgent problems have produced results as beneficial to the industry and to the consumers of rubber goods as the more fundamental studies of the causes and retardation of the deterioration of rubber.

Men who are well trained in research will seek and benefit by the unexpected. It is not sufficient, once a problem has been assigned, to assume that it will be subjected to all known methods of attack. New methods should be sought in the solution of baffling problems. The research director compliments the men on his staff when he gives them an opportunity to attempt the solution of a hard problem. The greatest inspiration to a competent investigator is the opportunity to meet the challenge of what Doctor Whitney has chosen to call the "inexhaustible unknown."

A group of scientists had been working diligently for months in the attempt to utilize a new thermoplastic material for hard molded articles, such as phonograph records. Gratifying progress had been made. Many hundreds of records had

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[1] National Bureau of Economic Research, "Recent Economic Changes," p. 115, McGraw-Hill, 1929.

been molded, tested, and found to have durability and to yield excellent reproduction of sound. Months of effort had been spent, however, in attempts to remedy the inherent surface tackiness of the product. This thermoplastic, when hot, stuck persistently to mill rolls, hot plates, and mold surfaces. It suddenly dawned on one of these men that, since the product adhered tenaciously to metal when hot, this disadvantage of the material for molding plastics might be turned to a useful advantage in the field of adhesion of rubber to metal. By thus making a virtue of necessity, there resulted a commercially and now widely used process for such rubber adhesion. The discovery of an inherent and invariable property of a new material, as in this instance, may open the avenue to a new development in a field quite remote from the objective as originally conceived.

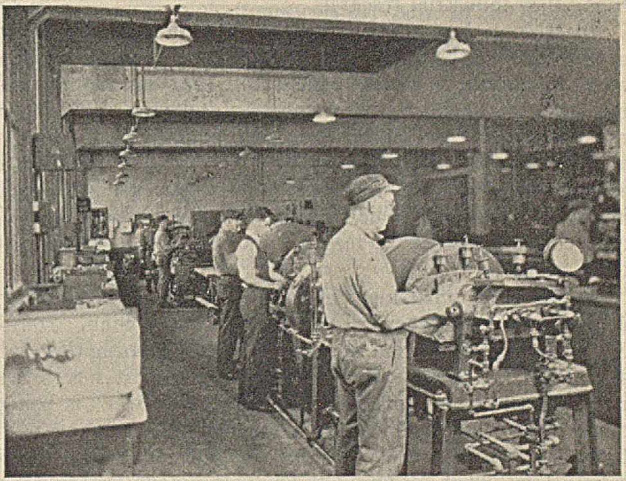
NECESSITY OF COÖPERATION BETWEEN MANAGEMENT AND RESEARCH DIRECTOR

One of the functions of the director of research is to keep his superiors informed concerning the strategic importance of key problems in the basic research program. The relation between such long-continued problems and the more immediate objectives which are continually being sought by industry requires vision on the part of both the management and the research director. Both types of problem should be studied simultaneously, but the temptation is continually present to reach for the immediate at the expense of the basic solution of studies which bear an intimate relationship to factory operation.

It is significant that the more simple and direct the type of supervision involved in the conduct of research, the more successful the whole undertaking is likely to prove. The prime function of organized research is not and cannot be interpreted to mean volume production in a given time. It is rather the sum total of creative effort of a number of individuals working independently, though coöperatively, in obtaining results from the unknown. A director of research who was asked by the production men on his executive committee just what he expected to realize from a large appropriation for research replied that he could not predict what results could be expected, because, if he could make such a prediction, the undertaking which he proposed would not be research. The constant objective of any worthy research undertaking should be to capitalize the unknown.

A man chosen for industrial research projects must possess a sincere enthusiasm for creative work. He should enjoy working with his hands as well as with his brain. It is understood that he must be dependable and have unquestioned scientific integrity and ability. The most favorable condition for the development of an investigator in industry is to assign him a problem which demands his best effort, both mental and manual, for its solution. He should be left as far as possible on his own resources, with only that necessary direction of effort which insures that he will become an integral part of the organization. Those responsible for directing his work need spend very little time in instructing a capable research man if they will but provide him with the facilities for his work and afford him the necessary human contacts for gathering information peculiar to the industry. It is frequently of great benefit to a research man in industry to be assigned a factory problem rather early in his career. It enables him to mesh gears with the large machine of which he is a part, and makes him feel the vital and immediate importance of science to industry. It furthermore enhances his understanding and appreciation of the production and sales viewpoints, and makes him realize that the management seeks and will speedily employ the proved results of scientific investigations.

In view of the intangible mental attributes which men must possess in order to become and to remain productive research workers, the management should recognize certain principles which constitute sound operating policy. Creative thinkers should be encouraged to originate and to elaborate new ideas. Since a productive worker is capable of originating ideas at a rate which exceeds his ability to elaborate them, junior assistants can frequently be provided with profit to the corporation. As material aids to research, suitable laboratories, a well-equipped library, chemical and apparatus stores, facilities for glass blowing and shop work, and a pilot plant for semiworks experiments constitute an irreducible minimum of necessary equipment. More important, however, than these material aids to progress is that abiding faith of the sponsor in the eventual success of research, which is typified by the recent action of the board of the International Nickel Company in providing an increased research appropriation as a logical corollary to the depression in business. Scientific men respond to an atmosphere of confidence on the part of management. Nature has imposed baffling and discouraging barriers to progress in research. Those companies which adopt the policy of recognizing successful effort by generous financial rewards are in the best position to profit quickly from the investment in scientific studies. The management can recognize and promote success by making special appropriations to support problems promising either large returns in the near future or results of large potential benefit in the long run. Such recognition of one phase of the research program spreads contagious enthusiasm among the workers in other projects. Scientific men cannot afford to be biased by petty personal jealousies, and they are stimulated to better output if they see their fellows, who have been successful, obtain merited recognition. Salaries commensurate with accomplishment are necessary both because they are deserved and in order to enable men to live without worry concerning their personal affairs. It is reasonable to suppose that any industry should be willing to reward the productivity of its research men on as generous a scale as they reward accomplishment in other divisions of the corporation.



EXPERIMENTAL PROCESSING UNIT OF B. F. GOODRICH CO.

TWOFOLD TEST OF RESEARCH

In a well-balanced research organization the test of excellence for the work of any individual is twofold. It involves his contributions either to scientific knowledge or to the benefit of the industry with which he is associated. No man who is productive in either sense is unsuccessful. It is but natural that some men will succeed best in fundamental research, whereas others will find their outlet in the handling of factory contact problems. Men will occasionally be found who succeed in both lines of endeavor. In a well-integrated research enterprise, both practical and theoretical talent are required and should be regarded and rewarded impartially by the laboratory management, strictly on the basis of constructive accomplishment.

Since the material benefit derived from research belongs to the employer and not to the employee, unless otherwise stipulated by agreement, it is the duty of the investigator to conduct his work in line with the interests of his company. This implies a willingness to subordinate motives of private gain or personal advantage to the welfare of the corporation as a whole. It does not, however, impose upon an employee the necessity of compromising his standing as a scientist or his scientific integrity, as is evidenced by the ever-increasing number of worthy scientific contributions by those who are engaged in industrial research.

Apart from the specific research program and the inner urge of the scientist to conceive and to elaborate new ideas, the research laboratory derives benefit from the suggestions originating in the operating departments of industry. The basic raw materials as well as the finished products of an industry are susceptible of improvement through research. Demands exist in every industry for lower costs, better products, and improved processes, which necessitate the maintenance of close contact between the research and the operating divisions of an industry.

The research department of an integrated unit of industry is analogous to the central nervous system of man. It receives the responses from the nerve endings, coördinating and stimulating ordinary activities; but above all it serves the reflective function, considers how best to do what is being done, what other products are available, what policy is best to pursue, why present activities and policies are not quite satisfactory, what by-products are being made that can be made to yield a profit, what the chances are that a particular product may be eliminated in competition, what outstanding properties fit the article of current manufacture for service, and what service is available that might better be rendered by a new product of manufacture. One large industry in recognition of the obvious advantages of free exchange of ideas, between research and production, has appointed men of mature research experience to serve as technical superintendents of major production divisions. This serves to place trained men in positions where they can encourage the application in production of results proved in research.

It also serves as the regeneration source of new ideas worthy of study and elaboration on the part of the research staff. The man who has had previous research training is a most valuable key man in either the production or the sales divisions of industry. He can visualize the opportunity for progress through improvement in both products and processes, and present the opportunity to those in charge of research. Such a policy requires of the research man more than a single-track mind, because the suggestion from other departments must be given intelligent and thoughtful consideration, and be related to the results of experiments in the laboratory. It is necessary for the research viewpoint to be combined with the engineering viewpoint in projects of this character.

Research management which fails to recognize that man is inherently gregarious in his instincts commits a blunder which is destructive to the spirit of research. To employ a man admittedly because he possesses a constructive curiosity and then to deprive him of one of the means of satisfying his curiosity—contact with others—is to destroy with one hand what the other attempts to create. A man is stimulated by exchange of views with other men who can impart pertinent information or constructive criticism.

When a problem has arrived at the development stage, the research man may in some cases participate in the reduction to practice of his own studies. In other instances the development division may conduct the factory trial. The research man in either case is entitled to know what factors contribute to the commercial success or failure of his ideas, since such knowledge is valuable to him in directing his further efforts.

CONCLUSION

Research is not an exotic organism requiring a protected environment for its existence. However, it thrives best in an industry in which active demands exist for its services. Where such demands have been demonstrated, it is incumbent upon those who formulate and guide research programs to stress fundamentals and to permit the investigators to exercise creative instinct. The enthusiasm and critical curiosity of the individual research worker is the best insurance of the success of the enterprise, and the type of organization which deliberately encourages original thinking on the part of its men will secure the largest benefits from research.

This encouragement and stimulation of original thinking can be accomplished best by the persistent support of fundamental studies by rewarding the research worker for constructive accomplishments, and by the prompt application of experimental results by the manufacturing divisions of the industry for the service of the public.

RECEIVED November 28, 1931.

THE LEAD INDUSTRY IN 1931. The lead industry in the United States in 1931 was severely affected by the depressed industrial conditions existing throughout the world, according to the Bureau of Mines.

Output of refined primary lead from domestic ores was 32 per cent lower than in 1930, following a decline of 15 per cent in 1930, and was the smallest recorded since 1910. Foreign primary output was 24 per cent lower than in 1930, following a drop of 32 per cent in 1930, and was the smallest recorded since 1921. The total refinery output of primary lead was 31 per cent below 1930, after dropping 17 per cent in 1930, and was the smallest since 1908. The quantity of lead indicated available for consumption in 1931 was the lowest on record since 1912, and represented a 29 per cent decrease from 1930.

The output of primary domestic desilverized lead in 1931 was about 206,000 tons; of soft lead about 143,000 tons, and of desilverized soft lead about 41,000 tons, making a total output from domestic ores of about 390,000 tons of refined lead. Corresponding figures in 1930 were 326,801 tons of desilverized lead, 201,361 tons of soft lead, and 45,578 tons of desilverized soft lead, making a total of 573,740 tons. The output of lead smelted and refined from foreign ore and bullion was about 53,000 tons, as compared with 69,293 tons in 1930. The total primary lead smelted or refined in the United States in 1931 was thus about 443,000 tons, a decrease of approximately 31 per cent as compared with the total of 643,033 tons in 1930. The output of primary antimonial lead in 1931 was about 9000 tons, as compared with 13,711 tons in 1930.

The average monthly price for lead at New York (outside market) was 4.80 cents a pound, the high for the year, during January. It dropped steadily to 3.82 cents in May, rose to 4.40 cents in July and August, and dropped steadily again to a low for the year of 3.80 cents in December. This is a repetition of the trend in 1930.

Occupations and Earnings of Chemical Engineering Graduates

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CHEMICAL ENGINEERING graduates have opportunity to use their professional training and are remaining in professional work. The men with master's degrees are distributed in industry in much the same proportions as those who entered industrial work immediately after graduation; the men with 2 or more years of graduate work show more pronounced differentiation.

It is apparent that the chemical engineering curriculum should plan to fit its graduates for research, plant development and operation, and general engineering, since 60 per cent of the graduates of 10 years ago are found in these fields. There can be no question but that these fields belong to the chemical engineer.

A study of salaries indicates that the chemical engineer fares somewhat better than the average engineer. The highest salaries are paid in the divisions of plant operation, general engineering, and sales.

THE information compiled in this paper was sought by the Committee on Chemical Engineering Education of the American Institute of Chemical Engineers as a help in the formulation of a better curriculum in chemical engineering. Since the purpose of any curriculum is to assist students to prepare for their life work, it is necessary to know the type of work which the graduates are to undertake after completion of their studies, and the paths by which they may expect to attain promotion before a curriculum may be intelligently designed. Much of the information in this paper was contained in a preliminary report presented to the Conference on Chemical Engineering Education held by the American Institute of Chemical Engineers at the University of Michigan, July 10 and 11, 1931.

Information could only be obtained through questionnaires, and, after consideration of cost, it was decided to restrict the number to about two thousand. The schools which coöperated in sending these questionnaires to their graduates were Massachusetts Institute of Technology, Brooklyn Polytechnic Institute, Ohio State University, University of Michigan, and University of Minnesota. They were selected as reasonably representative of both larger and smaller schools located in different sections of the United States. According to the figures of the Bureau of Education, these five schools enrolled 14 per cent of the total number of chemical engineering students in the United States in 1928.

The total number of questionnaires sent from the various schools was 2452, and the number returned in time to be tabulated was 1112, or 45.4 per cent of those sent out. The distribution of the questionnaires is shown in Table I.

Table I. Am. Inst. Chem. Eng. Questionnaires Returned and Tabulated

Michigan	378
Massachusetts Institute of Technology	318
Brooklyn Polytechnic Institute	58
Ohio State	231
Minnesota	127
Total	1112

It was at first intended to send only to those who graduated after 1919, but it was later decided to send to alumni graduating in the earlier years. This was done in the case of three of the schools. Some reference is made to the type of employment of the earlier graduates, but more attention is paid to the classes which graduated from 1920 to 1930. The information requested on the questionnaires was restricted to the 10 years following receipt of the first degree, partly because it was felt that the influence of curriculum had disappeared after that period and partly because of the expense of compilation of the data.

The information contained in the questionnaires was coded and transferred to punched cards which were tabulated mechanically. The card of each man carries a serial number, the name of the school from which he received his first degree, and the year of graduation, the same information for higher degrees, his type of employment, the industry with which he was connected, and the salary which he received for each of the first ten years. Information as to his official title was not transferred to the cards because it was found that the variety of titles was so great that it was difficult to reduce them to any system. The types of employment were coded as follows:

10	Graduate study
20	Teaching
30	Analytical laboratory
40	Research laboratory
50	Semi-plant development
60	Plant operation
70	General engineering
80	Sales
90	Consulting
91	Executive
92	Own employer
93	Military service
94	Miscellaneous
95	Not employed

The questionnaire asked that men whose time was divided between two different types of employment should indicate it by the use of the decimal 0.5, in the proper column. This information was transferred to the cards by use of the second figure in the code. For example, a man who was devoting half of his time to graduate study and half to teaching would have had his employment coded as 12, and one who was dividing his time about equally between the analytical laboratory and the research laboratory would have been given the code number 34. Salaries were coded to the nearest even hundred dollars. A man who reported his salary as $2140 was recorded as having a salary of $2100. Provision was made for tabulating separately those who, like graduate students, received no salary.

The Pre-War Situation

A preliminary study of the records of the earlier classes made it seem wise to omit the war years and also the very early years when the number of graduates was small. Information on the pre-war classes came only from the University of Michigan, the University of Minnesota, and Ohio State University. There were ninety-two questionnaries returned by graduates of the classes of 1910–15, and the only tabulation which has been made is that of the type of employment during the first year after graduation. The data are given in Table II. It will be noted that the analytical laboratory claimed over one-third of the total group, and that the plant (including development, operation, and general engineering) took only one-seventh of the total. Even in the pre-war days, over one-sixth of the number pursued graduate studies for at least 1 year.

TABLE II. TYPE OF FIRST-YEAR EMPLOYMENT, CLASSES 1910–15

	NO. OF INDIVIDUALS	PER CENT
Graduate study	15.5	16.9
Teaching	10.5	11.4
Analytical	34	36.9
Research	12	13.0
Semi-plant development	4	4.3
Plant operation	8	8.7
General engineering	1	1.1
Sales	4	4.3
Miscellaneous	3	3.4
Total	92	

It will be seen on comparing this result with that given in Table III for the class of 1921, or in Table IV which gives the data for the whole group graduating from 1920–30, that the graduates in these early years started, to a much larger extent, as analysts. Of this earlier group 36.9 per cent started as analysts as compared with 16.5 per cent of the classes from 1920–30. Only one-sixth of these earlier classes pursued graduate studies, whereas more than one-third of the later group devoted at least a year to graduate work. Only one-seventh of this pre-war group became immediately connected with larger scale development, but over one-third of the post-war group was employed in this manner.

TABLE III. TYPES OF EMPLOYMENT OF CHEMICAL ENGINEERS RECEIVING B. S. DEGREES IN ENGINEERING IN 1921

Year	1921	1922	1923	1924	1925	1926	1927	1928	1929	1930
Total individuals	75	77	78	79	77	79	78	77	78	68
Percentage in:										
Graduate study	37.4	12.4	11.6	8.9	3.2	0	0.6	0.7	0	0.7
Teaching	6.0	7.8	5.1	3.8	3.2	6.3	5.1	5.8	5.1	7.3
Analytical laboratory	16.7	22.0	17.3	13.3	9.8	7.6	7.7	3.9	4.5	5.2
Research laboratory	8.0	15.6	10.2	13.3	15.6	15.2	14.1	14.9	19.2	22.0
Semi-plant development	4.7	8.4	10.9	10.7	11.8	11.4	9.6	7.1	7.1	4.4
Plant operation	11.2	15.6	20.5	24.7	22.0	23.4	25.0	25.3	23.1	25.0
General engineering	10.7	7.8	10.2	10.2	14.9	11.4	13.6	11.8	12.8	12.6
Sales	0	1.3	2.6	4.4	8.4	9.5	10.2	14.2	14.1	12.6
Consulting	0	1.3	1.3	0.6	0.7	0	0	0.7	0	0
Own employer	1.3	1.3	2.6	2.5	3.9	5.1	6.4	6.5	5.1	2.9
Miscellaneous	4.0	6.5	7.7	7.6	6.5	10.1	7.7	9.1	9.0	7.3

POST-WAR DEVELOPMENTS AND THE CLASS OF 1921

The World War drew attention to the usefulness of chemical engineers, and subsequent to the war there was much more general appreciation of the value of specific training in chemical engineering. The curricula of the schools has undergone marked changes in the decade since the war, the principal developments being in the greater emphasis laid upon mathematics, physics, unit operations, and, in general, on the quantitative aspects of chemical-engineering operations. A study of the questionnaires of the classes graduating in the last decade should show if their present occupations indicate that they are in a position to make use of the information contained in these newer courses.

The type of employment of the class which graduated in 1921 is shown for each year in Table III. It will be observed that 37.4 per cent of the graduates returned for a year of graduate work, and that 12.4, 11.6, and 8.9 per cent of the total number remained in graduate work during the next 3 successive years, after which there was a sharp drop in the number reported as engaged in graduate study. In tabulating these figures, a student who reported that half his time was devoted to graduate work and half to teaching was reported as half a man in each group. Most of the students who spent more than 1 year in graduate work were also engaged in teaching, and therefore the number of graduates reported as teachers decreases during the first 4 years, as does the percentage of those enrolled as graduate students. The proportion of graduate students becomes substantially zero after 5 years, while the percentage of teachers jumps from 3.2 to 6.3 after the fifth year, indicating that some of the men who had continued to their doctorate as part-time teachers were now devoting their full time to teaching. The proportion of students in the analytical laboratory dropped steadily for 8 years from an initial figure of 16.7 to 3.9 per cent in the eighth year. A slight increase in this percentage appeared in the ninth and tenth years, which, however, is hardly significant, since it only means that one man changed his occupation each year to analytical work. The number of graduates of this class in the research laboratory shows a steady increase from 8.0 per cent the first year to 22.0 per cent in the tenth year. The number in semi-plant development shows an increase from 4.7 per cent in the first year to 11.8 in the fifth year, with a rather gradual decline during the next 4 years and a sudden drop the last year to 4.4 per cent. This probably means, that during the later years men were transferring to positions more directly associated with plant operation or to general engineering. The number of graduates in plant operation rose from 11.2 per cent in the first year to 24.7 in the fourth year and remained almost steady at that figure thereafter. The number who started in general engineering was 10.7 per cent, and, although there was some fluctuation and a gradual increase to 12.6 per cent, the percentage did not change much during the whole 10 years. There was none of this class of 1921 who engaged in sales work during his first year, but the numbers increased to 14.2 per cent at the end of 8 years and remained almost constant during the next 2 years. The number of individuals who are in consulting work is negligible, and the number who are their own employers is also small throughout. There is an apparent tendency for the numbers in this latter class to increase until 1929, with a sharp decrease in 1930. The heading "miscellaneous" includes all of the graduates who reported their type of employment, and who did not fit into any of the preceding eleven groups. It includes the men who have gone into other types of business, or who have entered other professions, and also includes those who stated they were unemployed for any year. The number in this latter group is astonishingly small, never rising to over 1 per cent. It may perhaps be surmised that the men out of employment glossed over the fact and omitted information for that year. When information for a year was blank, it was marked with an X and omitted from the tabulation. It will be noted that the number of individuals throughout the first 9 years stays between the figures 77 and 79, but drops to 68 in 1930. It may be that this means that ten men did not report what they were doing their last year. It is also possible that some of the men figured that, since they graduated in 1921, they had been out only 9 years in 1930 and therefore made a return for only 9 years. This would account for the drop in the numbers in the tenth year and seems an explanation which has considerable plausibility.

The general trend of this tabulation of data from the class of 1921 indicates that over one-third of the group entered graduate work, and that it was not until after 4 years that the full number of the group had connected themselves with industries. The 16.7 per cent of those who went at once after their first degree into the analytical laboratory was augmented to 22 per cent after 1 year by the men who had taken their M. S. degrees, and the 8 per cent, who entered the research laboratory at once after the first degree, grew to 15.6 per cent by additions from the same source. The groups that entered semi-plant development and plant operation probably grew by transfers from the analytical or research laboratories. At the end of the 10-year period the proportion in the analytical laboratory was only 5 per cent and that in the research laboratory 22 per cent, making 27 per cent who reported themselves in laboratory work. Those who reported themselves as directly connected with plant operation included 4.4 per cent in semi-plant development, 25.0 in plant operation, and 12.6 in general engineering, or 42.0 per cent directly connected with the plant. The sales division took 12.6 per cent of the graduates. It is significant that only 7.3 per cent are found under the heading "miscellaneous," which includes all those whose reports showed that they had severed direct connection with their chemical engineering work, as well as those still working as chemical engineers but in capacities not included in the groups.

TYPE OF EMPLOYMENT OF GRADUATES, 1920–30

The information which has been given concerning the class of 1921 is presented as an illustration of the material which has been compiled for each of the classes from 1920–30. There are rather minor differences in the grouping in the various classes, but the picture is so nearly the same that it has seemed entirely proper to combine the information from all classes into one table and then obtain the benefit of the truer picture resulting from the larger number of individuals in the group. The information for these eleven classes is presented in Table IV and shown graphically in Figure 1. The number of individuals varies from 771 in the first year after graduation to 120 in the tenth year, where only the classes of 1920 and 1921 can be included. There is a marked similarity between the distribution of the students of the class of 1921 and of the eleven classes from 1920–30. In each case over one-third of the students continued into graduate work, most of them remaining only for 1 year, and the balance dropping out rather more slowly during the 3 following years. The number of teachers fluctuates somewhat from year to year, but shows an increase after the fourth year to a final figure of 10.8 per cent. The number employed in the analytical laboratory shows a maximum of 16.5 per cent in the first year of employment and decreases rather rapidly until at the end of 6 years only 4.5 per cent are engaged in analytical work. The research laboratory employs 12.6 per cent of the graduates in the first year, but takes 18.6 the second year, the increase undoubtedly coming from the men who have received a master's degree. The proportion of men employed in the research laboratory stays relatively constant after the second year. Semi-plant development takes 7.1 per cent the first year and 13.6 per cent the second year, the increase again undoubtedly coming from the graduate students. The numbers in this division stay relatively constant for the next 3 years and then gradually decrease to 7.5 per cent. Plant operation takes 13.5 per cent of the men the first year, 17.9 the second year, and an increasing number during the following 2 years, after which the numbers remain substantially constant. It seems probable that the increasing group in plant operation is recruited in part from graduate students and in part from men transferred from the group on semi-plant development, who in turn may be recruited from men in the research laboratory. The general engineering group starts with only 4.9 per cent and increases to 11.7 after the tenth year. Very few of the graduates enter the sales division immediately after leaving college, only 1.8 per cent being recorded in the first year. The numbers gradually increase to a value of 13.8 in the seventh year, after which the figures stay relatively constant. The miscellaneous group starts with 4.2 per cent and increases for 8 years to 15.5 per cent.

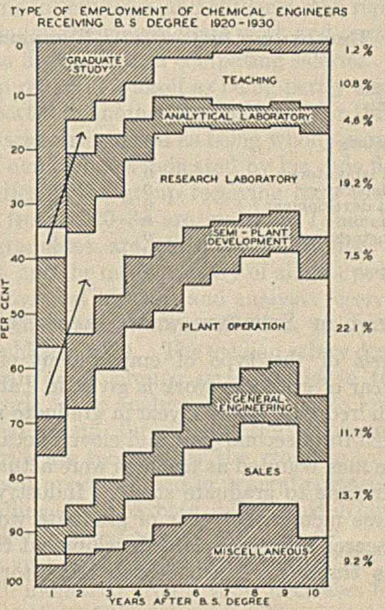

FIGURE 1

TABLE IV. EMPLOYMENT OF CHEMICAL ENGINEERS WITH B. S. DEGREE IN ENGINEERING (1920–30, INCLUSIVE)

Years after B. S.	1	2	3	4	5	6	7	8	9	10
Total individuals	771	705	630	567	498	431	352	288	195	120
Percentage in:										
Graduate study	34.2	14.5	10.8	7.6	3.3	3.2	2.0	1.0	1.5	1.2
Teaching	5.2	6.0	6.0	6.5	7.3	7.6	9.4	10.9	9.2	10.8
Analytical laboratory	16.5	14.2	11.4	7.6	5.9	4.5	4.7	3.5	3.8	4.6
Research laboratory	12.6	18.6	18.1	17.5	19.9	18.7	16.8	15.8	16.1	19.2
Semi-plant development	7.1	13.6	13.7	13.7	12.4	10.4	9.2	7.5	7.4	7.5
Plant operation	13.5	17.9	20.5	22.5	22.4	22.0	20.4	21.0	20.0	22.1
General engineering	4.9	6.1	6.8	8.8	8.3	8.1	10.5	9.4	11.5	11.7
Sales	1.8	3.0	5.2	6.8	9.5	12.4	13.8	15.5	14.9	13.7
Miscellaneous	4.2	6.1	7.5	9.1	10.8	13.0	13.2	15.5	15.4	9.2

This survey of the 1920–30 graduates indicates that there is considerable shifting during the first 5 years, due largely to the infiltration of graduate students during that period. After 5 years the groups are relatively stable, as shown in Table V. It will be noted that 43.1 per cent of the chemical engineers are directly connected with the plant, either in semi-plant development, plant operation, or general engineering, and that 19.9 per cent are in the research laboratory.

TABLE V. EMPLOYMENT OF 1920–30 GRADUATES AFTER 5 AND 10 YEARS

	AFTER 5 YEARS	AFTER 10 YEARS
Total individuals	498	120
Graduate study and teaching	10.6	12.0
Analytical laboratory	5.9	4.6
Research laboratory	19.9	19.2
Semi-plant, plant operation, and general engineering	43.1	41.3
Sales	9.5	13.7
Miscellaneous	10.8	9.2

Table VI. Employment of Chemical Engineers with B. S. Degree in Engineering, Followed by 1 Year of Graduate Work (1920–30, Inclusive)

Years after B. S.	1	2	3	4	5	6	7	8	9	10
Total individuals		261	227	209	182	162	137	107	72	48
Percentage in:										
Graduate study	100	31.8	20.3	12.4	3.0	2.8	1.9	0.9	2.8	2.1
Teaching	0	11.3	12.8	11.5	11.5	11.7	13.9	16.4	12.5	12.5
Analytical laboratory	0	10.3	9.3	6.7	4.9	3.1	3.6	1.4	1.4	2.1
Research laboratory	0	18.2	18.1	18.4	24.5	25.6	23.7	19.6	24.3	29.2
Semi-plant development	0	12.8	14.1	13.9	13.7	11.4	10.6	8.9	5.6	4.2
Plant operation	0	9.4	13.8	18.2	20.6	19.1	16.4	16.4	16.0	16.7
General engineering	0	2.3	4.8	7.4	7.4	5.6	9.1	10.3	13.9	12.5
Sales	0	1.7	3.8	5.5	7.7	11.4	12.0	13.6	9.7	8.3
Miscellaneous	0	2.1	3.1	6.0	6.6	9.3	8.8	12.6	13.9	12.5

Table VII. Employment of Chemical Engineers with B. S. Degree in Engineering, Followed by 2 Years of Graduate Work (1920–30, Inclusive)

Years after B. S.	1	2	3	4	5	6	7	8	9	10
Total individuals			93	84	69	62	52	38	28	17
Percentage in:										
Graduate study	100	100	45.2	23.8	3.6	2.4	1.9	1.3	3.6	0
Teaching	0	0	16.1	17.3	21.7	21.0	25.0	27.6	25.0	29.4
Analytical laboratory	0	0	5.4	1.8	1.4	1.6	..	..	..	..
Research laboratory	0	0	16.1	21.4	33.3	34.7	34.6	31.6	32.1	35.3
Semi-plant development	0	0	8.1	15.5	17.4	13.7	13.5	11.8	5.4	..
Plant operation	0	0	4.3	8.3	8.7	12.1	8.7	6.6	8.9	5.9
General engineering	0	0	2.7	4.8	5.8	3.2	7.7	7.9	14.3	23.3
Sales	0	0	1.1	1.2	2.2	3.2	1.9	5.3	3.6	..
Miscellaneous	0	0	1.1	6.0	5.8	8.1	6.7	7.9	7.1	5.9

Employment of Students with Graduate Training

An analysis of the type of employment of those who pursued 1 year of graduate work is given in Table VI. Out of every hundred who spent 1 year in graduate work, thirty-two continued for a second year and eleven became teachers. Many of the men counted as teachers were actually devoting part of their time to graduate study. Industry apparently regarded these men with 1 year of graduate work as better fitted for research and semi-plant development than the men without this training. The research laboratory took 18.2 per cent during their first year of industrial work, the semi-plant development 12.8 per cent, and plant operation 9.4 per cent of the group. The figures for those who had been out of school 4 years showed that 24.5 per cent were in the research laboratory, 13.7 per cent in semi-plant development, and 20.6 in plant operation. The reports from those who had received a bachelor's degree 10 years earlier show that 29.2 per cent were in the research laboratory, 16.7 in plant operation, and 12.5 in general engineering.

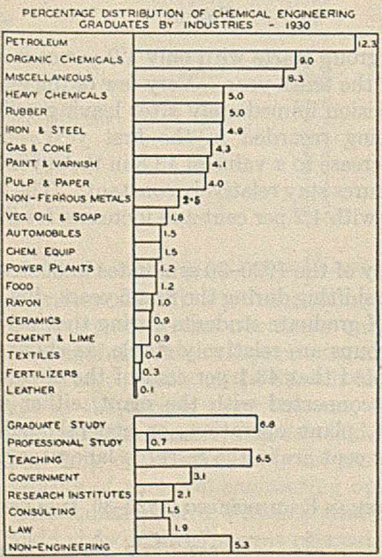

Figure 2

Nearly half of the men who took 2 years of graduate work continued for a third year and presumably took doctors' degrees. The data given in Table VII show that the group reporting their occupations 5 years after receiving bachelors' degrees contained 21.7 per cent engaged in teaching, 33.3 in research, and 17.4 in plant development. The group reporting after 10 years shows 29.4 per cent engaged in teaching, 35.3 in research, and 23.5 in general engineering. An extraordinary feature of these questionnaires is the very small number of the graduates who do not fall into one of the categories which have been discussed. These are all grouped in Tables IV, V, VI, and VII under the heading "miscellaneous," whose total never rises over 15.5 per cent. This is discussed later in the article.

Distribution of Graduates by Industries

The preceding discussion of the questionnaires has dealt with the classification of chemical engineers according to type of employment. The information on the questionnaires is also adequate to study the distribution of the graduates by industries as it varies from year to year. On account of the expense of tabulation, the only study that has been made of these data has been that of the distribution of the 10 classes 1920–29 by industries, as reported for the single year 1930. The data given in Table VIII and shown graphically in Figure 2 cannot be compared with those of Table IV, showing the distribution of the graduates by type of employment, since they are on an entirely different basis. Table IV gives a picture of what all of the graduates of the 10 years did in their first and in succeeding years. Table VIII gives the industrial affiliations of the whole group of graduates for the 10-year period as they were in 1930.

The figures of Table VIII have been arranged in two groups. The first contains 29.0 per cent of the questionnaires and is made up of those still engaged in study, and those teaching, working for governments or research institutes, in consulting practice, in law, and in miscellaneous occupations. The second group contains 71.9 per cent of the questionnaires and includes all reporting themselves as connected with specific industries. In studying the distribution of the engineers in this latter group, it is noted that petroleum employs the greatest number, followed by organic chemicals; heavy chemicals; rubber; iron and steel; gas and coke; paint, varnish, and lacquer; and pulp and paper, in the order named, each industry taking 4 per cent or more of the total number of graduates. If the number engaged in the industries applying organic rather than inorganic chemistry be totaled, it is found that 44 per cent of all of the graduates, or 61 per cent of all those directly connected with industry, are working in the organic field.

The first group of Table VIII, listing those not directly connected with industry, shows the graduate students as the largest unit with 6.8 per cent of the total, followed by teachers, government employees, and workers in research institutes in the order named. Consultants comprise only 1.5 per cent of the total and are surpassed in number by the lawyers with 1.9 per cent.

TABLE VIII. 1930 DISTRIBUTION OF CHEMICAL ENGINEERING GRADUATES

(Recipients of B. S. degrees in 1929–30, inclusive)

INDUSTRY	NO.		PERCENTAGE	
Graduate study	46		6.83	
Professional study	5		0.74	
Teaching	44		6.52	
Government (national, state, city)	21		3.12	
Research institutes	14		2.08	
Consulting practice	10		1.48	
Law	13		1.93	
Engineering other than chemical	10		1.48	
Outside of engineering	36		5.34	
		199		29.52
Petroleum	83		12.30	
Organic chemicals	61		9.01	
Miscellaneous	56		8.30	
Heavy chemicals	34		5.04	
Rubber	34		5.04	
Iron and steel	33		4.90	
Gas and coke	29		4.30	
Paint, varnish, and lacquer	28		4.15	
Pulp and paper	27		4.00	
Non-ferrous metals	17		2.52	
Vegetable oil and soap	12		1.78	
Automobiles	10		1.48	
Chemical equipment	10		1.48	
Power plants and public utilities other than gas	8		1.19	
Food	8		1.19	
Rayon	7		1.04	
Ceramics	6		0.89	
Cement and lime	6		0.89	
Textiles (natural)	3		0.44	
Fertilizers	2		0.30	
Leather	1		0.15	
		475		70.39
Total		674		99.91

A surprising feature of this table is the small number of those reported as outside of engineering—only 5.3 per cent. This includes all who could not be classified in one of the other divisions of the table, even those who reported themselves as unemployed. Some comment was made earlier on the small number whose employment did not fit into the framework of Table IV, and the two tables are in general agreement on this point. If the figures of Table VIII could be taken at face value, it would mean that nearly 95 per cent of all the chemical engineering graduates were employed where they were presumably using their professional training. The figure is impossibly high, but the only way to discount it is to assume that a large proportion of those who failed to reply to the questionnaire did so because they had left the field of chemical engineering and were not sufficiently interested to send in the information requested. There is no evidence to support this latter hypothesis and no way to tell what the real figures should be.

TABLE IX. SALARIES OF CHEMICAL ENGINEERS

(Data from graduates receiving B.S. degrees in engineering, 1920–30)

YEARS AFTER FIRST DEGREE	TEACHING		ANALYTICAL LABORATORY		RESEARCH LABORATORY		SEMI-PLANT DEVELOPMENT		PLANT OPERATION		GENERAL ENGINEERING		SALES		ALL GROUPS		TOTAL INDIVIDUALS
	A[a]	B[b]	A	B	A	B	A	B	A	B	A	B	A	B	A	B	
1	$1500	$1800	$1600	$1800	$1800	$1800	$1800	$2000	$1800	$1800	$1800	$1800	$1800	$1800	$1800	$1800	417
2	1600	1900	1800	2000	2000	2400	2000	2400	1900	2200	1800	2100	2200	2500	1900	2200	493
3	1800	2100	2000	2200	2200	2700	2300	2600	2300	2700	2400	2600	2400	2700	2200	2500	455
4	1900	2400	2100	2500	2500	3000	2400	2800	2500	3000	2700	3000	3000	3300	2400	2900	413
5	2100	2600	2400	2700	2700	3200	2800	3300	2800	3300	3100	3600	3300	4200	2700	3300	382
6	2400	2600	2600	2900	3200	3600	3000	3700	3200	3400	3400	3700	3600	4500	3000	3600	317
7	2700	2800	2900	3100	3300	4000	3300	3600	3300	4400	3600	4200	4100	5400	3300	3900	255
8	2800	3000	3300	3600	3600	4000	3400	3600	3900	4500	3800	4600	4600	5400	3600	4200	202
9	3000	3200	3300	3600	3900	5000	3600	4500	4100	5000	3600	4800	5000	7000	3900	4800	135
10	3200	3700	3000	4500	3800	5400	3400	4000	4000	4500	4100	7000	5500	7200	4100	5000	101

[a] A = median

[b] B = lower limit of upper quartile

The information is definite that 94.6 per cent of the 674 chemical engineers who filled out the questionnaires are still in occupations which are presumably giving them an opportunity to use their professional training.

SALARIES OF CHEMICAL ENGINEERS

The salaries reported in the questionnaire vary from some which are very small up to one which was stated as $700,000. It is evidently impossible to use average figures, and median figures are substituted. In making the tabulation, salaries which were not reported at all were thrown out. Graduate students came in this class, and students who reported themselves as doing part-time graduate work and part-time teaching were also disregarded in computing salaries. In general, where a man reported himself as being partly engaged in one group and partly in another, he has been, for this purpose of studying salaries, considered as being wholly employed in the first type of employment indicated by his code figures. The median salaries of the group receiving their first degrees in engineering from 1920–30 are given in Table IX. In this table the graduates are classified according to type of employment, and the median salary of all groups is also given. It will be noted that teachers and analysts receive the lowest salaries, teachers being worse off than analysts until the tenth year, which is 1930. The median salary during the first year is $1800 for all groups except those in teaching and analytical work. The analysts remain in the lowest class of the industrial group throughout the whole period. The highest salaries are received by the group in sales, with the groups in plant operation and in general engineering ranking next, and pulling ahead of those in the research laboratory and semi-plant development work after 7 years.

The tenth year on this chart is the year 1930. The median salaries of all industrial groups show decreases for this year, with the exception of those in general engineering and sales, whose incomes have apparently increased materially. The income of the teachers also increases in 1930. The median salary for the combined groups is slightly higher than that reported by the Society for the Promotion of Engineering Education (*2*). The median salaries for over five thousand engineers was there reported to be $1800 at the end of the first year, $2800 after the fifth year, and $4000 after the tenth year.

If the salaries of those employed as teachers and analysts be excluded, the figures for the 5- and 10-year periods become significantly higher. The median salary of those employed in the divisions closely related to chemical engineering at the end of 5 years becomes $3100 instead of $2700, and after ten years, $4200 instead of $4100. The quartile salaries become $3600 instead of $3300 at the end of 5 years, and $5400 instead of $5000 at the expiration of 10 years.

The salaries of the men on the lower edge of the upper quarter in salary are also included in Table IX. The number of individuals in this upper quartile is too small to expect a smooth curve to result, but it is apparent that the differences

Table X. Salaries of Chemical Engineers with 1 Year of Graduate Work

(Data from graduates receiving B. S. degrees in engineering, 1920–30)

Years after First Degree	Teaching		Analytical Laboratory		Research Laboratory		Semi-Plant Development		Plant Operation		General Engineering		Sales		All Groups		Total Individuals
	A[a]	B[b]	A	B	A	B	A	B	A	B	A	B	A	B	A	B	
1	Graduate study		...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
2	$1500	$1800	$1800	$1800	$2100	$2500	$1800	$2100	$1800	$2000	$1800	$1900	$2200	$2200	$1800	$2100	146
3	1800	2200	2000	2200	2400	2700	2400	2600	2100	2400	2400	2500	2500	3800	2100	2400	154
4	2000	2500	2200	2500	2600	3200	2400	3000	2400	3000	2900	3000	3500	4000	2400	3000	151
5	2200	2800	2300	2700	2700	3100	3000	3600	3000	3600	3300	3500	3600	4700	2800	3300	155
6	2500	2700	2600	2900	3300	4000	3300	4000	3300	3800	3600	3700	3600	4700	3300	3800	137
7	2700	2800	2500	3400	3600	4000	3300	4000	3600	5100	3900	4200	4600	6000	3600	4100	115
8	2800	3000	[c]	[c]	3900	4300	3600	3900	4000	4700	4300	4600	4900	6000	3600	4500	88
9	3000	3200	[c]	[c]	4600	5100	4100	4300	4500	5000	4800	4800	5500	9000	4200	5000	57
10	3100	4300	[c]	[c]	4600	5400	[c]	[c]	4800	5000	5200	7500	5300	7500	3800	5000	43

[a] A = median

[b] B = lower limit of upper quartile

[c] Too small a group to be significant

Table XI. Salaries of Chemical Engineers with 2 Years of Graduate Work

(Data from graduates receiving B. S. degrees in engineering, 1920–30)

Years after First Degree	Teaching		Analytical Laboratory		Research Laboratory		Semi-Plant Development		Plant Operation		General Engineering		Sales		All Groups		Total Individuals
	A[a]	B[b]	A	B	A	B	A	B	A	B	A	B	A	B	A	B	
1	Graduate study		...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
2	Graduate study		...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
3	$1600	$2200	$1800	$2100	$2200	$2700	$2600	$3100	$2000	$2700	$2300	$2500	$1800	$1800	$2000	$2400	39
4	2500	2700	2200	2300	2500	3000	3000	3200	2000	2800	3000	3000	3300[c]	3300[c]	2500	3000	51
5	2500	3000	2300[c]	2300[c]	2700	3000	3300	3600	2400	3300	2000[c]	2000[c]	3600[c]	3600[c]	2700	3300	57
6	2500	2800	2600[c]	2600[c]	3300	3600	3000	4000	3000	4800	0	0	3000	3600	3000	3600	50
7	2700	2800	0	0	3500	4000	3500	4100	4500	6000	3500[c]	3500[c]	4000[c]	4000[c]	3500	4000	41
8	2900	3200	0	0	3900	4000	3600	4500	3600	4200	4100[c]	4100[c]	4200	4500	3600	4100	30
9	3000	3300	0	0	4600	5800	4500[c]	4500[c]	4200	5000	4900	5000	0	0	3600	4800	21
10	3000	4600	0	0	5400	6200	0	0	3600	3600	5200	5300	0	0	3800	5300	14

[a] A = median

[b] B = lower limit of upper quartile

[c] Only one in this group

are slight in the first year and increase as the individuals become older. The differences in the teaching profession and among the analysts are small, but they become most pronounced in the fields of general engineering and sales.

SALARIES AS AFFECTED BY GRADUATE STUDY

The salary schedules of men with 1 and 2 years of graduate work are recorded in Tables X and XI. The teachers do not show any financial benefit from either 1 or 2 years of graduate study, which may perhaps be accounted for by saying that promotion in the teaching profession tends to be largely through seniority. The explanation may also be that those who have not enrolled for formal graduate work have nevertheless taken advantage of the opportunities for study which are around them. The analysts also fail to show any financial returns for their graduate work, but very few men with graduate training stay long in the analytical laboratory.

The research division does not seem to repay the graduate student for his expenditures during the first few years of his industrial connection, but in later years the greater earning power of those with graduate work is established; in the tenth year the median salaries become $3800, $4600, and $5400 for those with no graduate work, 1 year, and 2 years, respectively.

The semi-plant division shows a higher salary, even at the beginning, for the men with 2 years of graduate work, but the number remaining in later years is too small to make the figures significant. The plant division actually penalizes the man with graduate work by not paying him much more than the starting wages of the man who began work directly after receiving his bachelor's degree. The men with masters' degrees who are in plant operation, pass those with bachelors' degrees in the fifth year, and those with two years of extra study reach the top of the list in the seventh year when the median salaries are $4500, $3600, and $3300 for the three classes. The men with 2 years of graduate study drift out of plant work apparently into general engineering, so that there are too few of them at the end of the tenth year to permit comparisons. Those in this division with 1 year of graduate work are, however, faring better ($4800) than those who had only their first degree ($4000).

The general engineering division recognizes the superiority value of graduate training by higher compensation in the fifth year. This division is one which attracts an increasing proportion of those with graduate training as they grow older and in the tenth year the median salary for the man without graduate training is $4100 as compared with $5200 for those who spent 1 or 2 years in further study.

The sales division does not seem to offer superior opportunities to men with graduate training, which is, on the whole, what might be anticipated.

DO CHEMICAL ENGINEERS BECOME EXECUTIVES?

The questionnaires upon which this report is based requested information as to the titles of those who responded. The replies to this part of the questionnaire were, however, so fragmentary and the titles reported so diverse that it has not seemed feasible to draw many definite conclusions from them. The analysis of the statistics of the class of 1921 shows that the percentage of those who were their own employers rose gradually to 6.5 in 1928 and dropped to 2.9 in 1930. The number who reported themselves as consulting engineers is negligible throughout. If the title of executive is restricted to general officers of corporations, then very few chemical engineers attain it within 10 years after graduation. Chemical engineers are usually employed by large corporations, and it is too much to expect that many men will rise to become general managers or vice presidents of such organizations within a decade after leaving college. If, however, an executive is defined as one who guides and directs others in important projects, then there is abundant evidence that many, even of those out of college only a few years, are in executive positions. The owners of those creative minds which make possible new processes and products, and which supervise their development and production are truly executives whose influence molds policies and who are influential in bringing prosperity—or depression—to their employers. A questionnaire sent to

Table XII. Summary of Enrollments in 145 Engineering Schools in U. S., 1930–31 (*1*)

Curricula and Courses	Freshmen	Sophomore	Junior	Senior	Total Under-graduate	Graduate	Others	Grand Total	Per Cent of Total
Electrical	6662	4768	3973	3162	18,565	790	637	19,992	25.4
Mechanical	5322	4217	3287	2227	15,053	343	288	15,684	19.9
Civil	4452	3563	3154	2644	13,813	333	388	14,534	18.5
Chemical	3433	2567	1877	1277	9,154	400	113	9,667	12.3
Mining and metallurgy	940	712	647	472	2,771	129	44	2,944	3.7
Architectural	821	820	657	542	2,840	42	58	2,940	3.7
Aeronautical	695	591	462	255	2,003	45	9	2,057	2.6
General	521	252	473	172	1,418	16	3	1,437	1.8
Chemistry	272	201	179	143	795	384	167	1,346	1.7
Architecture	335	286	268	249	1,138	47	7	1,192	1.5
Industrial	278	375	263	233	1,149	8	5	1,162	1.5
Business and administration	279	253	161	144	837	8	1	846	1.1
Petroleum	218	192	153	81	644	44	3	691	0.9
Ceramics and ceramic engineering	177	163	109	108	557	37	33	627	0.8
Textile	119	69	70	37	295	1	34	330	0.4
Miscellaneous	808	602	529	415	2,354	312	570	3,236	4.1
Total	25,332	19,631	16,262	12,161	73,386	2939	2360	78,685	

these same men after another decade would undoubtedly show a much larger proportion as general officers of corporations, for there is an evident trend in industry to recruit the higher administrative staff from the ranks of men with professional training.

Future Demand for Chemical Engineers

The demand for chemical engineers during the prosperous years of 1924–29 was much greater than the supply. The subsequent depression caused a sharp decrease in the demand and brought unemployment to a considerable number. What does the future offer?

The number of chemical engineering students in the United States has increased rapidly in recent years. Statistics compiled by John of the Bureau of Education (*1*) and summarized in Table XII show that in the year 1930–31 there were 9667 students following curricula definitely labeled "chemical engineering," and that they formed one-eighth of the total students in colleges of engineering. There were other smaller groups following curricula labeled "petroleum" with 691 students, ceramics with 627, and textiles with 300 which are evidently very closely related to chemical engineering. There was also a larger group in mining and metallurgy with 2944 students who, in so far as they become metallurgists, will enter chemical engineering fields. The number of seriors in chemical engineering proper was 1277. The number of freshmen shown in this same table was 3433, and it may be expected that from them there will be in 1934 about 1600 graduates from the courses labeled "chemical engineering," with several hundred additional coming from the more specialized but closely related curricula. This is a large number to be absorbed by industry, and the question may well be raised as to whether industry can use so many new recruits profitably.

A partial answer to this question may be found in data compiled by the Committee on College Employment of the American Management Association, from questionnaires submitted to companies in selected lines of industry. Their final report has not yet been made public but permission has been given to quote from their preliminary statement, from which the data in Table XIII have been taken. The figures obtained from the questionnaires were multiplied by a factor representing the ratio of the number of employees in companies reporting, to the total number of employees in that branch of industry; and the committee emphasizes that the table "represents a potential and not an actual demand, but it does represent what would occur if all of the companies in these industries were employing graduates at the rate of those replying to the questionnaire." The report of the American Management Association discusses the demand for various kinds of engineers, but space does not permit referring to any but chemical engineers in this paper.

The figures in Table XIII represent the potential annual demand for chemical engineers in eight industries. Four of these industries—iron and steel, petroleum products, chemicals and allied products, and food products—are clearly chemical industries and, according to the table, should call for 750 chemical engineering graduates every year. The other four industries making reports are distinctly not chemical industries—electric light and power, electrical communications, electrical manufacture, and machinery manufacture—and it is perhaps a matter of surprise that they indicate a potential demand for 165 chemical engineers annually. These eight industries, therefore, have a presumptive capacity for 915 chemical engineering graduates annually, which is about 80 per cent of the total number who graduated in 1931.

Table XIII. Probable Annual Demand for Chemical Engineers

(Extract from report of Committee on College Employment of American Management Association)

Industry	Total Employees	Annual Requirement for Chemical Engineering Graduates
Electric light and power	300,000	20
Electrical communications	475,000	20
Electrical manufacture	300,000	65
Iron and steel	960,000	130
Petroleum products	80,000	145
Chemicals and allied products	250,000	400
Food products	830,000	75
Machinery manufacture	750,000	60
Total		915

What is the probable demand by other industries which were not included in the eight groups to whom questionnaires were sent by the American Management Association? The Census Bureau divides the industries into sixteen groups, listed in Table XIV in the same order as that followed by the Bureau. This table also gives the number of wage earners in each group of industries and the value added by manufacture, as furnishing the best indication of the contribution which the manufacturing organization has made by its work. The third column gives the percentage of chemical engineering graduates now employed by these industries, as shown by the present questionnaires and reported in Table VIII.

The industrial groups of the American Management Association correspond in general to those of the Census, in so far as chemical engineers are concerned. The four groups listed by the American Management Association as employing large numbers of chemical engineers—iron and steel, petroleum products, chemicals and allied products, and food products—employ, according to the questionnaires, 41.6 per cent of the chemical engineers now in industry. This may indicate a potential demand at the present time for over twice as many men as are called for in the groups reported by the American

Management Association, or approximately two thousand new recruits to industry each year.

An inspection of Table XIV indicates that nearly all of the industries are potential fields for chemical engineers, and that some of them are absorbing only a small fraction of the number indicated by the number of employees and the value of their products. The food, textile, and leather industries are cases particularly in point. It is perhaps idle to speculate too much on the future possibilities for chemical engineers, but the figures indicate that the saturation point is still some distance in the future.

TABLE XIV. CENSUS STATISTICS OF MANUFACTURES, 1927

(Compared with percentage of chemical engineers employed by specific industries)

INDUSTRIES	WAGE EARNERS	VALUE ADDED BY MANUFACTURE	CHEMICAL ENGINEERS EMPLOYED
	1000	*$1,000,000*	%
Food and kindred products	680	2902	1.19
Textiles and their products	1694	4028	0.44
Lumber and allied products	863	1823	...
Paper and paper products	226	715	4.00
Printing, publishing, and allied industries	328	2094	...
Chemicals and allied products	253	1594	23.24
Products of petroleum and coal	142	798	16.60
Rubber products	142	565	5.04
Leather and its manufactures	316	781	0.15
Stone, clay, and glass products	350	1018	1.33
Iron and steel, and their products	836	2654	4.90
Non-ferrous metals and products	271	888	2.52
Machinery	886	3305	1.48
Transportation equipment (air, land, water)	495	1786	1.48
Railroad repair shops	429	1744	...
Miscellaneous	441	1935	...

SUMMARY

The figures presented have answered rather definitely the query which caused the preparation of the questionnaires. Chemical engineering graduates have opportunity to use their professional training and are remaining in professional work. The statistics of the classes graduating between 1920–30 indicate that 16.5 per cent of the graduates enter the analytical laboratory, but only one-third of them are left in that division after 5 years; that 12.6 per cent start in the research laboratory, and that the number is increased to 18.6 per cent after 1 year, largely by additions of students with 1 year of graduate training, and stays relatively constant during the later years; that 7.1 per cent start in semi-plant development, and that the proportion is increased by influx of students with the master's degree to 13.7 per cent in the second year, a figure which remains relatively constant for 3 years and then slowly declines. Plant operation takes 13.5 per cent of the men immediately after graduation and an increasing proportion of the total group until the fifth year, when a level of 22.5 per cent is reached. General engineering starts with less than 5 per cent of the men with the bachelor's degree, and adds to the numbers slowly and progressively until 11.7 per cent of the total are found in that division. Sales follows a similar curve, starting with 1.8 per cent and ending with 13.7.

Over one-third of the students graduating between 1920–30 remained for at least 1 year of graduate work, and 40 per cent of that group remained for at least 1 more year of study.

The men with masters' degrees do not distribute themselves very differently from those who entered industrial work immediately after graduation. A larger proportion of them (24.5 as compared with 17.5) are found in the research laboratory in the fifth year after graduation, and a somewhat smaller proportion (20.6 as compared with 22.4) are in plant operation. There are relatively fewer of these men in the analytical laboratory, in sales, and in general engineering.

The men with 2 or more years of graduate work show more pronounced differentiation. Five years after the bachelor's degree, 21.7 per cent are in teaching, 33.3 in research, 17.4 in semi-plant development and only 8.7 in plant operation. The group reporting 10 years after graduation shows 29.4 per cent in teaching, 35.3 in research work, and 23.5 in general engineering. These three divisions account for 88.2 per cent of the total group. It may perhaps be assumed that the more intellectual students continue for 2 years of graduate work and find their most attractive fields in teaching, research, and general engineering.

It is apparent that the chemical engineering curriculum should plan to fit its graduates for research, plant development, and operation, and general engineering. Sixty per cent of the graduates of 10 years ago are found in these four fields, and, if those who have gone into teaching or outside fields are excluded, the proportion rises to 75 per cent. Over 80 per cent of the men who took 2 years of graduate work and did not go into teaching are found in the two fields of research and general engineering. The sales division attracts a material number of chemical engineers as they get older, but there is nothing to show that the curriculum influences their choice or that graduate study improves their opportunities in this field.

There can be no question but that the fields of plant development, operation, and engineering belong distinctively to the chemical engineer. There may be some ground for debate as to the proper training of men for the research division. There is certainly room for men with varied training in research, and in some organizations plant development is carried in the research divisions. The questionnaires show that research is an attractive and profitable field for an important proportion of the chemical engineering graduates, especially if they have graduate training.

A study of salaries indicates that the chemical engineers fare somewhat better than the average engineer. The poorest paid groups are the teachers and those in the analytical laboratories. The highest salaries are paid in the plant operation, general engineering, and sales divisions. The men with graduate training pass those without this advantage in the research, plant operation, and general engineering fields. The situation at the end of 10 years is shown in Table XV.

TABLE XV. SUMMARY OF EARNINGS OF CHEMICAL ENGINEERS 10 YEARS AFTER RECEIVING B. S. DEGREES

(As influenced by graduate training)

	AMOUNT OF GRADUATE TRAINING					
	None		1 Year		2 Years	
TYPE OF WORK	A[a]	B[b]	A	B	A	B
Research	$3800	$5400	$4600	$5400	$5400	$6200
Plant operation	4000	4500	4800	5000	...	...
General engineering	4100	4700	5200	7500	5200	5300

[a] A = median salary

[b] B = upper quartile salary

The number of chemical engineering students in the colleges has grown rapidly, and in 1930–31 there are 1277 seniors following curricula in chemical engineering. The numbers in the freshman classes indicate that in three years there may be 1700 seniors. It is notoriously unsafe to prophesy, but from the statistics presented it seems probable that even this number will find employment during periods of normal business activity. Almost all of the large industries have need for chemical engineers, either in large or small numbers. Some of them are just awakening to their needs, and it is in these as yet undeveloped fields that many of the future chemical engineers will find their spheres of activity.

LITERATURE CITED

(1) John, W. C., *J. Eng. Education*, 22, 56 (1931).
(2) Soc. Promotion Eng. Education, Repts. Investigation Eng. Education, *Bull.* 3, 262.

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Heat Content of Petroleum-Oil Fractions at Elevated Temperatures

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THE TOTAL HEAT of five oils, in both liquid and vapor phases, has been determined at temperatures up to 540° C. (1004° F.). Four of these oils were of Midcontinent source and had densities ranging from 0.747 to 0.934 (20° to 58° A. P. I.). The data obtained for these four oils have been incorporated into two equations, one for vapors and the other for liquids, which are recommended for Midcontinent source oils. The fifth oil studied was a highly refractory gas-oil stock, which had a history of many passages through cracking units, and was probably entirely different in chemical constitution from cuts direct from crude oil. The data for this oil are compared to those for the other oils as a gage of the variation in total heat which may occur with an oil of widely different constitution.

The effect of pressure on the total heat of a naphtha vapor has been investigated for certain pressures and temperatures. Certain determinations of critical temperatures are reported.

DATA relating to the heat content of petroleum fractions at high temperatures, in both liquid and vapor phase, are among the tools most frequently used by the designer of petroleum equipment. Heretofore, these high-temperature data have rested upon extrapolation of the many investigations made in the range of temperature between 0° C. (32° F.) and perhaps 350° C. (662° F.). Since most of the modern equipment in which oil is distilled, and all of that in which it is cracked, operates far above the maximum temperature of previously published investigations, it seemed worth while to study experimentally the heat-content relationships in this highly interesting temperature range.

The present paper gives the results of this work with selected characteristic fractions of petroleum vapors and liquids up to about 540° C. (1004° F.). A critical survey of the literature on the subject has been made, and certain of these literature data combined with the low- and high-temperature findings of the present authors to form the basis of curves. These curves present what is believed to be the best existing published data on the heat content of oils, as liquid or vapor, in the temperature range of 0–540° C. (32–1004° F.), and as a function of their density (0.966–0.74 specific gravity or 15–60 A. P. I. gravity).

Previous workers have been content to limit their determinations of heat content or specific heat of oil fractions to temperatures below that at which decomposition (cracking) is commonly supposed to occur. It is well known, however, that cracking is proportional to the product of some function of time, and another function of temperature. Certain types of commercial distillation equipment are designed with this relationship in mind, the effort being to heat the oil to the required temperature quickly, and to cool it below the range of rapid decomposition before significant chemical changes can occur. This desired result is frequently obtained to an extent which makes it difficult to show, by usual physical tests of quality, that any decomposition whatever has occurred. The experimental equipment with which these high-temperature heat-content data were secured was designed to provide a very rapid sequence of heating and cooling effects, and the decomposition of the oil under the most severe conditions was found to be so small as to affect the results to a negligible extent only.

Details of the experimental equipment and the mode of operation will be given in the last section of this paper under Experimental Equipment and Method. For the present it need only be stated that the stream of oil was heated continuously by passage through a tube in an electric-resistance heated furnace. Means to hold any desired pressure on the oil passing through the furnace were provided, together with a sampling connection so that a small portion of the hot-oil stream could be diverted to a vacuum-jacketed calorimeter. The major portion of the oil was wasted to a condenser cooler of conventional type. At the start of an experiment the calorimeter, a silvered vacuum bottle of the thermos type, was packed with granular ice below 0° C. This ice was completely melted in the approximate 4-minute duration of an experiment, during which time 100–350 grams of hot oil were introduced into the calorimeter. The heat content under any given condition was calculated from a knowledge of the initial temperature of the oil, the heat equivalent of the calorimeter and fittings, the weight and temperature of the ice at the start and of both water and oil at the conclusion of an experiment.

Seven oils were used in the experimental work. Their character is indicated by the data in Table I.

Table I. Physical Characteristics of Stocks Investigated[a]

	Naphthas			Refined	Gas Oils		Lubricating-Oil
	A	B	C	Oil	A	B	Stock
Sp. gr. at 60° F.	0.7483	0.7475	0.7459	0.8203	0.8504	0.9639	0.9334
A. P. I. gr.	57.6	57.8	58.2	41.0	34.9	15.3	20.1
Amount over A. S. T. M. Distillation Method			Temperatures				10 mm. Hg Pressure
%	° F.	° F.	° F.	° F.	° F.	° F.	
Initial	140	108	105	359	514	396	292
1	155	122	116	363	524	416	348
3	172	137	129	372	534	428	372
5	179	148	139	378	540	438	388
10	192	170	157	387	549	454	413
20	211	200	186	399	564	472	445
30	226	227	211	410	574	484	473
40	239	251	235	419	582	488	503
50	252	272	259	428	593	500	531
60	268	293	281	439	604	514	565
70	288	313	303	451	618	532	603
80	317	331	319	464	636	564	654
90	361	359	353	482	668	620	...
95	430	388	375	494	690	...	...
Dry	487	406	409	513	...	700	700
% Off	98	97	98.5	98	95	94	88

[a] All of these stocks, except gas oil B, were cuts from Midcontinent-type crudes obtained in pipe-still distillation and under what the refiner calls "non-cracking" conditions. No doubt these oils represent mixtures which are not radically different from similar boiling mixtures of truly original components of the crude. On the other hand, gas oil B had a history of many passages through cracking units under the most drastic conditions and bears no resemblance in chemical constitution to its original source.

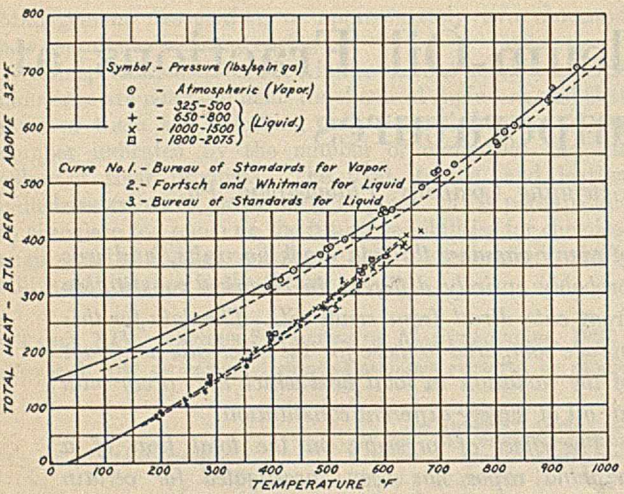

Figure 1. Data on 58° A. P. I. Naphtha
(Including comparison with literature)

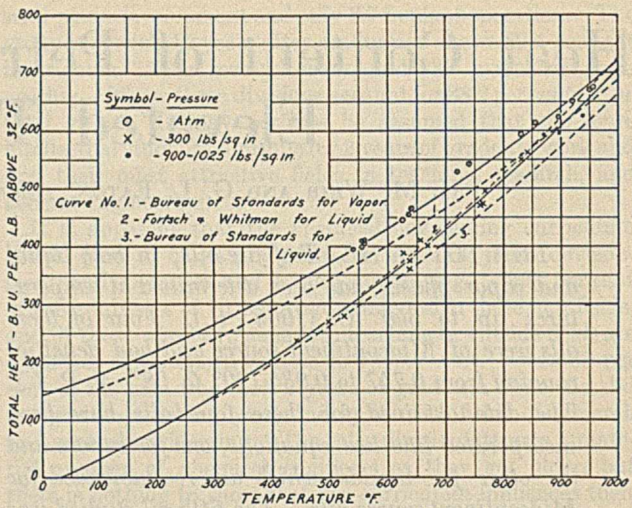

Figure 2. Data on 41° A. P. I. Refined Oil
(Including comparison with literature)

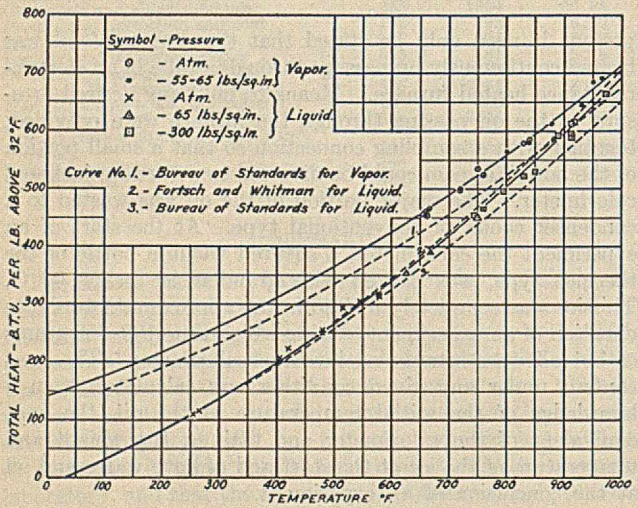

Figure 3. Data on 34.9° A. P. I. Gas Oil
(Including comparison with literature)

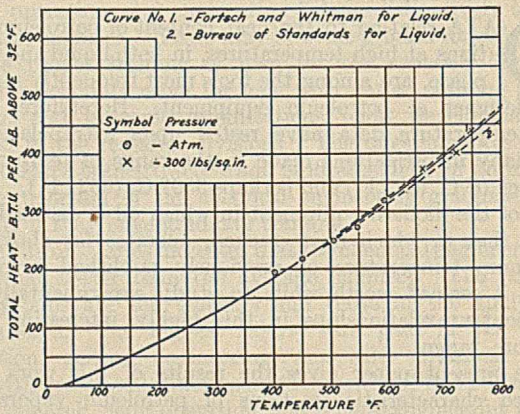

Figure 4. Data on 20.1° A. P. I. Lubricating Oil
(Including comparison with literature)

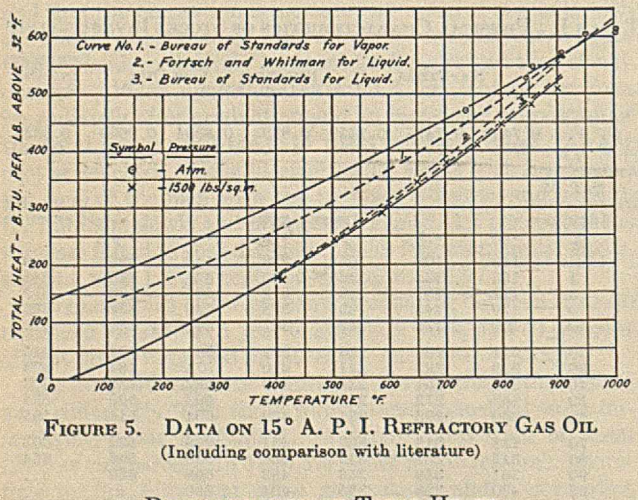

Figure 5. Data on 15° A. P. I. Refractory Gas Oil
(Including comparison with literature)

Determination of Total Heats

Vapor Phase. The heat of these materials in the vapor phase was determined at substantially atmospheric pressure. The effect of pressure on the heat content of one of the naphthas, C, in the vapor phase, was also determined at several pressures, including a maximum of 2000 pounds per square inch, by observation of the magnitude of the Joule-Thomson effect, i. e., the temperature change on adiabatic expansion of the gases.

Liquids. The heat content of the liquid state *vs.* temperature, for the several stocks, was determined at various pressures, dictated by the physical properties of the particular oil. For any given experimental temperature, the pressure maintained was greater than the vapor pressure of a pure paraffin hydrocarbon having a boiling point equal to the initial point of the particular material being studied, as determined by the A. S. T. M. distillation. The vapor pressure–temperature relation was determined according to the method suggested by Cox (*4*).

It was felt that this procedure would assure conditions under which no vaporization would occur at the point where the temperature was read, and before release of oil to the calorimeter.

Correlation of Data

Some two hundred and thirty satisfactory determinations were made in the course of the work. The essential data appear in Table II and the results are shown graphically in Figures 1 to 5. The solid curves on each of these figures are the weighted or "best" lines through the data points.

TABLE II. EXPERIMENTAL DATA OBTAINED IN HEAT-CONTENT DETERMINATIONS

NAPHTHA (58.0° A. P. I.)[a]

TEMP. °F.	PRESSURE Lb./sq. in.	INITIAL ICE TEMP. °F.	FINAL MIX TEMP. °F.	WEIGHT OF ICE Grams	WEIGHT OF OIL Grams	HEAT CONTENT ABOVE 32° F. B.t.u./lb.	HEAT CONTENT CORRECTED FOR COOLING, ABOVE 32° F. B.t.u./lb.	DEVIATION FROM CURVE %
949	Atm.	19.4	51.4	363.7	89.3	705	...	+1.1
903	Atm.	18.7	65.5	328.4	94.9	668	...	+1.2
896	Atm.	26.0	112.5	390.1	153.1	646	...	−1.2
835	Atm.	16.0	115.0	393.9	173.0	601	...	−1.0
817	Atm.	22.0	123.0	393.3	181.4	590	...	−0.6
804	Atm.	3.5	57.0	208.9	71.1	567	...	−2.9
801	Atm.	23.5	117.0	177.6	86.5	572	...	−1.6
727	Atm.	16.0	78.0	397.8	159.6	532	...	+0.8
713	Atm.	7.5	53.6	328.0	117.5	518	...	0
698	Atm.	19.4	42.8	264.3	82.0	522	...	+2.8
696	Atm.	10.2	57.2	370.0	133.9	517	...	+2.1
669	Atm.	19.0	98.0	392.4	192.7	492	...	+0.8
615	Atm.	23.0	59.5	407.2	167.0	451	...	−0.3
603	Atm.	10.0	86.7	276.0	144.7	448	...	+0.7
600	Atm.	17.6	49.6	280.9	108.6	450	...	+1.6
596	Atm.	6.8	43.5	336.4	128.3	445	...	+1.1
530	Atm.	20.0	78.0	403.0	216.6	398	...	−0.5
503	Atm.	22.3	70.5	266.1	139.9	385	...	+0.5
500	Atm.	17.4	59.5	199.6	99.1	384	...	+0.7
487	Atm.	21.0	47.5	380.3	174.4	372	...	−0.5
438	Atm.	26.0	67.5	417.8	238.2	344	...	−0.6
414	Atm.	19.0	81.0	341.6	232.1	327	...	−1.8
393	Atm.	31.0	92.0	384.6	285.3	314	...	−2.5
289	340	14.7	82.0	168.5	281.3	157	145	+0.7
284	325	21.2	84.0	222.2	374.7	153	142	+0.7
280	350	11.3	40.3	193.2	243.9	137	126	−8.7
252	325	17.2	66.2	161.3	288.6	128	120	0
247	330	9.7	55.8	198.2	376.4	111	104	−11.5
242	340	28.4	47.1	209.7	300.8	122	115	+0.9
202	325	15.8	44.2	193.6	388.6	91	89	−1.1
192	325	27.0	48.2	197.2	415.7	87	86	+1.8
200	400	14.9	56.6	146.2	344.7	92	90	+1.0
520	500	23.0	122.0	343.0	318.2	316	291	...
450	500	31.0	82.0	363.3	300.0	267	242	−4.1
415	500	20.0	94.0	371.2	383.1	244	220	−3.3
360	500	23.0	59.0	397.6	373.3	204	183	−3.7
353	500	27.0	60.0	249.2	253.0	191	171	−7.6
288	500	26.0	48.0	355.4	402.2	154	142	−0.7
362	650	24.5	91.4	189.2	230.9	213	192	+0.3
347	675	14.4	66.5	214.9	226.7	205	185	+1.9
352	800	9.4	60.0	188.0	188.6	203	183	−0.9
400	1000	19.0	57.0	256.1	189.0	254	230	+6.0
489	1225	16.1	84.0	173.0	137.4	304	278	−1.1
478	1300	23.9	52.2	295.0	174.2	302	276	+1.1
667	1500	20.0	123.0	411.9	273.4	426	413	...
640	1500	17.0	98.0	394.4	230.6	421	406	...
637	1575	19.5	133.0	343.9	259.9	406	391	...
633	1500	17.0	46.5	392.0	167.1	402	385	...
607	1500	26.0	69.0	314.6	160.2	391	371	...
580	1500	31.0	75.0	411.0	227.2	369	347	...
558	1500	29.0	39.0	374.9	166.1	349	325	...
505	1500	26.0	101.5	247.0	199.9	320	294	...
494	1500	22.0	69.0	320.7	213.0	300	274	−3.9
490	1500	16.0	77.0	275.4	200.4	302	276	−2.1
442	1500	12.0	71.0	257.4	201.4	275	250	+1.2
395	1500	25.0	75.0	357.3	326.7	236	212	−0.9
370	1500	31.0	67.0	406.4	359.9	224	202	+2.5
309	1500	6.0	142.0	56.3	187.7	170	156	−0.3
602	2000	1.0	38.0	272.9	118.3	389	368	...
578	2050	28.4	77.9	206.9	116.1	385	363	...
565	1800	16.5	38.0	190.9	79.7	371	348	...
561	2000	12.0	61.0	213.9	116.9	361	338	...
555	2000	9.0	38.0	183.7	82.3	366	342	...
555	2075	24.4	106.8	208.2	166.8	339	315	...
404	2000	11.0	61.0	191.3	153.1	253	229	+4.1
398	2000	11.0	88.0	275.4	282.1	245	221	+2.3
396	2000	15.0	47.0	133.7	93.4	253	229	+6.7
288	2000	15.0	67.0	165.7	219.5	166	154	+7.7

Average deviation of vapor from curve = 0%
Average deviation of liquid from curve = −0.3%

[a] First 23 runs, vapor phase; other runs, liquid phase.

REFINED OIL (41.0° A. P. I.)[b]

TEMP. °F.	PRESSURE Lb./sq. in.	INITIAL ICE TEMP. °F.	FINAL MIX TEMP. °F.	WEIGHT OF ICE Grams	WEIGHT OF OIL Grams	HEAT CONTENT ABOVE 32° F. B.t.u./lb.	DEVIATION FROM CURVE %
957	Atm.	30	51	350.5	87.7	675	−1.5
950	Atm.	23	61	367.9	101.7	671	−1.3
920	Atm.	22	111	376.1	146.4	651	−0.8
896	Atm.	22	68	403.9	126.2	624	−2.2
855	Atm	21	64	421.9	149.0	614	+1.3
830	Atm.	21	79	426.0	150.6	595	+1.2
740	Atm.	19	106	414.3	190.9	543	+3.8
720	Atm.	24	144	388.0	225.0	529	+3.9
640	Atm.	22	80.8	362.6	168.1	466	+2.2
635	Atm.	29.5	40.8	375.4	128.8	456	+0.3
625	Atm.	22	69	385.2	170.5	446	0
560	Atm.	20	99	381.3	230.8	405	−0.2
560	Atm.	20	97	387.4	228.1	411	+1.2
555	Atm.	22	35	381.5	146.3	399	−1.0
555	Atm.	22	86	410.5	224.7	409	+1.5
540	Atm.	25.5	104	378.1	239.6	395	+0.2
841	300	21	116	418.2	194.8	563	+2.0
830	300	24	94	416.2	173.0	551	+1.7
768	300	17	63	406.5	158.6	496	+2.0
763	300	26	60	412.6	159.5	474	−1.5
759	300	23	142	383.6	250.4	471	−1.5
668	300	25	130	365.8	265.3	401	−0.2
656	300	15	64	431.7	205.3	411	+4.8
637	300	20	80.7	411.8	237.9	375	−0.3
637	300	16	62.7	388.9	210.7	360	−4.2
627	300	27	38	411.0	163.2	389	+5.4
523	300	15	59	423.7	291.4	279	−3.5
497	300	18	55	413.6	283.7	269	−0.4
442	300	30	61.5	414.0	328.9	237	+2.2
938	1025	31	50.5	388.5	103.8	625	−2.8
897	925	16	89.5	397.3	152.3	596	−1.3
870	900	28	84.5	422.4	151.3	594	+2.6

Average deviation of vapor from curve = +0.5%
Average deviation of liquid from curve = +0.3%

[b] First sixteen runs, vapor phase; other runs, liquid phase.

GAS OIL (34.9° A. P. I.)

TEMP. °F.	PRESSURE Lb./sq. in.	INITIAL ICE TEMP. °F.	FINAL MIX TEMP. °F.	WEIGHT OF ICE Grams	WEIGHT OF OIL Grams	HEAT CONTENT ABOVE 32° F. B.t.u./lb.	DEVIATION FROM CURVE %
840[c]	Atm.	2	134	331.5	171.4	586	−0.3
830[c]	Atm.	9	115	362.2	168.1	580	0
760[c]	Atm.	10	72	357.6	142.9	524	−0.9
750[c]	Atm.	12	66	379.0	141.0	536	+2.5
720[c]	Atm.	12	82	403.1	178.7	500	−0.5
720[c]	Atm.	7	46	428.5	151.2	499	−0.7
667[c]	Atm.	5	70.5	323.9	147.0	467	0
662[c]	Atm.	4	59	382.8	165.5	453	−2.4
660[c]	Atm.	3	108.5	438.5	252.3	462	−0.1
655[c]	Atm.	4	68	387.1	176.1	457	−0.5
580[d]	Atm.	7	38.5	424.3	225.1	314	−3.1
578[d]	Atm.	1	65	294.9	197.0	316	−1.9
578[d]	Atm.	4	129	248.4	253.1	319	−0.9
545[d]	Atm.	6	89	378.3	301.1	307	+3.0
515[d]	Atm.	7	114	405.2	395.6	294	+6.1
480[d]	Atm.	19	95.5	265.5	265.4	257	+2.0
480[d]	Atm.	9	96	312.7	327.5	251	−0.4
420[d]	Atm.	6	85.8	227.5	257.7	224	+5.9
405[d]	Atm.	6	57.8	253.7	247.5	208	+3.2
265[d]	Atm.	5	36.2[e]	265.2	334.5	116	−0.4
255[d]	Atm.	10	34.6[e]	252.6	310.0	111	0
950[c]	60	15.5	91.7	379.6	127.7	685	+2.0
930[c]	55	14.5	56	378.5	108.0	646	−1.5
878[c]	60	7	76.5	331.3	117.7	612	−0.6
840[c]	60	24	79	385.4	139.0	580	−1.2
800[c]	65	18	86	408.2	160.1	566	+1.4
750[d]	65	21	72	356.1	161.0	451	−1.7
668[d]	65	25	59	400.3	188.2	391	−0.4
625[d]	65	9	90.5	358.9	244.3	355	−0.8
965[c]	275	28	110	398.2	142.0	692	+1.2
890[d]	275	32	73	369.6	122.4	593	+1.4
973[d]	300	21	86	398.1	131.6	663	−0.3
918[d]	300	26	69	431.6	136.0	615	+0.7
912[d]	300	21	85	393.9	140.4	612	+1.2
912[d]	300	30	123	377.7	169.2	596	−1.5
912[d]	300	28	55	393.8	117.2	589	−2.6
850[d]	300	24	70.5	453.2	168.9	530	−3.3
830[d]	300	29	101	431.6	195.3	523	−1.3
795[d]	300	15	93	406.5	192.0	497	−0.4
760[b]	300	16	98.5	388.5	203.3	466	−0.4
745[b]	300	16	156	425.9	314.7	453	−0.4

Average deviation of vapor from curve = −0.1%
Average deviation of liquid from curve = +0.1%

[c] Vapor phase. [d] Liquid phase. [e] Refers to grams of ice unmelted.

LUBRICATING STOCK (20.1° A. P. I.)[f]

TEMP. °F.	PRESSURE Lb./sq. in.	INITIAL ICE TEMP. °F.	FINAL MIX TEMP. °F.	WEIGHT OF ICE Grams	WEIGHT OF OIL Grams	HEAT CONTENT ABOVE 32° F. B.t.u./lb.	DEVIATION FROM CURVE %
595	Atm.	31.5	60	441.4	252.1	318	+1.0
548	Atm.	22.0	74	365.6	282.0	273	−2.8
506	Atm.	17.0	85	377.9	351.6	249	−1.6
452	Atm.	26.0	86	405.4	434.2	217	−0.2
403	Atm.	24.0	69	399.4	421.1	195	+4.0
722	300	23.0	143	391.0	304.0	400	−2.3
663	300	22.0	98	406.8	263.3	373	+2.5

Average deviation from curve = +0.1%

[f] Liquid phase.

Table II. Experimental Data Obtained in Heat Content Determinations (*Concluded*)

Temp.	Pressure	Initial Ice Temp.	Final Mix Temp.	Weight of Ice	Weight of Oil	Heat Content above 32° F.	Deviation from Curve
° F.	*Lb./sq. in.*	*° F.*	*° F.*	*Grams*	*Grams*	*B.t.u./lb.*	*%*
			REFRACTORY GAS OIL (15.3° A. P. I.)[g]				
1003	Atm.	22	49	411.4	112.2	613	−1.9
1002	Atm.	25	52	386.5	107.8	607	−2.9
950	Atm.	26	53	429.5	121.6	604	+1.7
906	Atm.	16	66	375.7	125.6	582	+2.4
856	Atm.	22	60	380.2	127.2	548	+1.5
844	Atm.	16	73	335.8	130.4	528	−0.9
738	Atm.	20	63	302.3	123.2	471	+0.9
900	1500	20	45	381.3	123.2	508	...
854	1500	16	52	364.7	133.7	481	...
800	1500	13	68	395.1	177.0	447	+0.2
757	1500	14	57	369.2	166.6	410	−0.7
702	1500	15	60	368.7	184.1	379	+1.7
650	1500	20	64	327.4	183.1	345	+2.4
588	1500	16	53	322.9	199.3	291	−1.2
502	1500	22	87	364.2	346.7	244	+2.1
410	1500	14	34.5	315.1	278.2	174	−5.4
403	1500	18	45	364.9	334.7	178	−1.1

Average deviation of vapor from curve = +0.1%
Average deviation of liquid from curve = −0.2%

[g] First seven runs, vapor phase; other runs, liquid phase.

Temp.	Pressure	Initial Ice Temp.	Final Mix Temp.	Weight of Ice	Weight of Oil	Heat Content above 32° F.	Deviation from Curve
			STEAM[h]				
1000	Atm.	24.0	123.0	400.4	67.8	1573	+3.4
982	Atm.	18.0	56.2	408.0	48.9	1517	+0.3
920	Atm.	28.0	70.0	397.7	50.7	1516	+2.2
835	Atm.	25.5	80.0	429.8	61.8	1447	+0.2
715	Atm.	23.5	86.5	438.2	68.1	1401	+1.0
701	Atm.	7.0	76.5	257.1	41.3	1390	+0.7
635	Atm.	20.0	72.0	410.0	59.4	1389	+3.0
610	Atm.	18.0	75.0	396.6	59.5	1378	+3.0
600	Atm.	5.0	87.0	247.9	44.0	1330	−0.2
550	Atm.	24.0	62.0	426.2	59.6	1330	+1.5
515	Atm.	16.0	65.0	444.3	68.5	1281	−0.9
507	Atm.	−1.0	110.0	247.1	52.1	1305	+1.2
401	Atm.	−1.0	109.0	218.0	47.8	1255	+1.2
365	Atm.	30.0	61.0	403.1	59.1	1239	+1.3
320	Atm.	32.0	85.0	380.4	66.1	1225	+1.9

Average deviation = +1.3%

[h] Vapor phase.

SUMMARY OF DATA ON EFFECT OF PRESSURE ON TOTAL HEAT (58° A. P. I. NAPHTHA)

Pressure at Valve Block *J*	Pressure, Calorimeter *S*	Temp. in Valve Block *J* Thermocouple *K*	Temp. in Valve Block *J* Thermocouple *Y*	Calorimeter Temp. Thermocouple *T*	Calorimeter Outlet Temp. Thermocouple *X*	Temp. Change from Block *J* to Calorimeter *S*
Lb./sq. in.	*Lb./sq. in.*	*° F.*	*° F.*	*° F.*	*° F.*	*° F.*
3.5	0	650	653	654	642	+ 4
0	0	745	750	747	736	+ 2
0	0	848	847	854	836	+ 6
4.5	0	949	951	947	931	− 2
100	0	650	654	640	629	−10
100	0	750	753	739	725	−11
100	0	850	851	837	821	−13
100	0	945	948	927	908	−18
200	0	751	753	730	718	−21
200	0	853	856	830	816	−23
200	0	955	957	933	915	−22
400	0	853	853	809	795	−44
400	0	949	953	913	895	−36
800	0	946	949	887	871	−59
750	5	944	936[i]	887	874	−57
750	0	844	841	780	768	−64
400	0	846	845	806	795	−40
750	0	745	737[i]	668	660	−77
400	0	749	741[i]	707	697	−42
750	0	668	665	567	560	−101
750	0	673	668	570	565	−103
400	0	674	670	628	622	−46
200	0	674	680	645	638	−29
200	0	675	675	646	639	−29
600	0	672	671	589	582	−83
400	0	622	622	561	554	−61
600	0	621	621	509	504	−112
750	0	621	621	497	493	−124
400	0	570	579	470	467	−100
600	0	575	579	433	428	−142
750	0	575	577	435	431	−140
600	0	752	740[i]	685	676	−67
600	0	846	839[i]	790	779	−56
1450	0	844	840	751	743	−93
1050	0	846	839[i]	768	757	−78
1450	0	744	738[i]	634	626	−110
1050	0	749	745	648	639	−101
1450	0	674	668[i]	547	541	−127
1050	0	670	661[i]	553	546	−117
1450	0	623	617[i]	490	485	−133
1050	0	623	614[i]	488	485	−135
1450	0	573	569	425	422	−148
1050	0	574	567[i]	428	425	−146
2000	0	548	547	390	387	−158
2000	0	522	514[i]	354	351	−168
2000	0	497	494	323	320	−174
400	0	947	950	920	908	−27
1450	0	937	946	867	852	−70
1050	0	947	945	891	879	−56
200	0	551	531[i]	514	507	−37
400	0	549	545	426	423	−123

[i] Unreliable value due to small amount of naphtha flowing past thermocouple *Y*.

SUMMARY OF DATA (STEAM)

Pressure at Valve Block *J*	Pressure in Calorimeter *S*	Temp. in Valve Block *J* Thermocouple *K*	Temp. in Valve Block *J* Thermocouple *Y*	Calorimeter Temp. Thermocouple *T*	Calorimeter Outlet Temp Thermocouple *X*	Temp. Change from Valve Block *J* to Calorimeter *S*	Calcd. Temp. Change
Lb./sq. in.	*Lb./sq. in.*	*° F.*	*° F.*	*° F.*	*° F.*	*° F.*	*° F.*
90	2	750	754	748	738	−2	−14.6
90	2	800	803	796	785	−4	−15.1
90	2	900	905	895	883	−5	−12.6
90	2	1002	1002	995	980	−7	−10.6

It will be noted that no determinations of total heat were made in the region of low temperatures. Accordingly, the statement that the solid curves are "best" lines through the data needs amplication.

It should first be observed that the dotted curves on each figure correspond to the relationship of heat content of liquid *vs.* temperature, calculated from specific-heat data of Fortsch and Whitman (*5*), and a Bureau of Standards publication (*2*). Furthermore, the dotted line showing the heat content of vapor *vs.* temperature corresponds to calculation of this factor according to the same Bureau of Standards publication.

Although the Fortsch and Whitman equation was applied far above that justified by their experiments (where specific heat of the liquid was measured only to 554° F.), inspection shows that it represents most of the liquid data fairly well. Coincidence of the present authors' best lines with that of Fortsch and Whitman in the lower temperature ranges is obtained by the simple extrapolation of these best lines to 0° F., assuming that the relationship is parabolic. In the zone of higher temperature, where data were obtained in this work, the solid-line extensions were determined by continuing the best parabolic curves through the data. That is, the best straight lines through data points plotted on the coördinates, H/t-32 and t (° F.), were determined by the method of averages.

The curves so obtained can be incorporated into a single relationship, Equation 1, which is recommended for calculating the liquid heat content of Midcontinent-source oils:

$$H = (15d - 26) - (0.465d - 0.811)\,t + 0.000290t^2 \quad (1)$$

where H = total heat content above 32° F., B. t. u. per lb. of oil
t = temperature, ° F.
d = sp. gr. of material as liquid at 60° F.

The solid or best vapor heat-content lines were calculated, using Bahlke and Kay's equation (*1*) for the specific

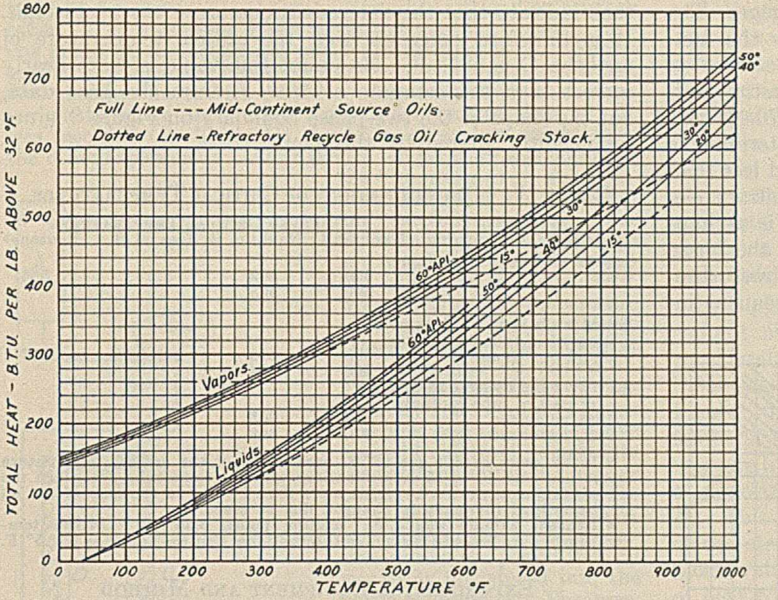

FIGURE 6. TOTAL HEAT *vs.* TEMPERATURE FOR MIDCONTINENT CUTS IN LIQUID AND VAPOR PHASES

heat of petroleum vapors. When integrated this equation becomes:

$$H = K + (0.415 - 0.104d)t + (0.000310 - 0.000078d)t^2 \quad (2)$$

where K = constant of integration (i. e., heat content of vapor at 0° F.)

On choosing appropriate values of K, it was found that this equation coincided almost exactly with the best line through data of the present writers for the naphtha, refined oil, and gas oil in a temperature range far exceeding the experimental data obtained by Bahlke and Kay, whose maximum temperature was 662° F. (350° C.).

The extrapolation of these vapor heat-content lines over a range of several hundred degrees back to the origin of abscissas (0° F.) could not be justified at all were it not for the fact that the slopes of these lines are thus known for a range of nearly 1000° F., and the position fixed by the average of determinations in the upper several-hundred-degree range. As it stands, no great accuracy can be claimed for the total heat curves on vapors more than 100° F. or lower than the range of actual experimentation, but it is probable that the extrapolation is as good as any attempted calculation in which data on pure compounds are utilized together with the Clausius-Clapeyron relationship.

Like the liquid data, it was found possible to incorporate the vapor heat content *vs.* temperature relationship in a single recommended equation for Midcontinent oil vapors, involving the nomenclature already given.

$$H = (215 - 87d) + (0.415 - 0.104d)t + (0.000310 - 0.000078d)t^2 \quad (3)$$

In order to make the data on the heat content of the liquids and vapors convenient to apply to other Midcontinent oils, total heat curves were calculated for intervals of even 5 or 10 A. P. I. degrees to form Figure 6 for data in the liquid and vapor phases.

The so-called 15 A. P. I. dotted curve on Figure 6 was not calculated with the above equation but simply reproduces the data on the refractory gas oil, B.

Gas oil B was chosen because of its extreme variance from the Midcontinent-type oils upon which the bulk of the work was done. The results obtained in its case are presented both as a rough gage of the possibility of applying the Midcontinent data to other types of oil, and as a picture of the behavior of refractory cracking stocks.

EFFECT OF PRESSURE ON HEAT CONTENT OF VAPORS

Aside from the interest which attaches to the determination of the Joule-Thomson effect from a theoretical standpoint—namely, for calculation of co-aggregation and co-volume constants in gas equations, it is of immediate practical application, since immense quantities of petroleum are daily vaporized under considerable pressure. It is unfortunate that time did not permit investigation of the Joule-Thomson effect on all vapor for which calorimetric data were obtained. The experimental work, which was confined to naphtha, was practically complete when it was learned that Bahlke and Kay were to present results on the same type of investigation of a naphtha vapor before the meeting of the AMERICAN CHEMICAL SOCIETY in September, 1931. Through the courtesy of these workers the present authors have been able to inspect certain of their curves, showing their data which apparently agree well with present findings, considering the generic nature of the term "naphtha." At this writing the details of the work of Bahlke and Kay are unknown to the writers, so that further reference cannot be made.

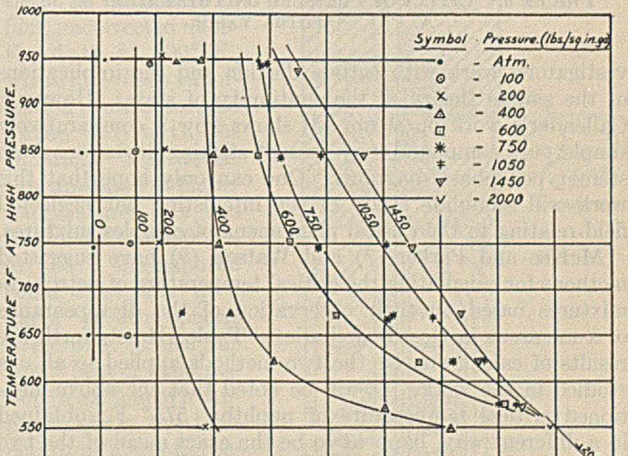

FIGURE 7. TEMPERATURE CHANGE ON ADIABATIC EXPANSION OF 58° A. P. I. NAPHTHA VAPOR

In determining the effect of pressure on vapor heat content of naphtha, the present writers used a throttling calorimeter according to the method detailed in the next section of this paper. Figure 7 presents the data obtained (see also Table II) on the temperature decrease occasioned by continuous adiabatic expansion of vapor from several known high temperatures and pressures to atmospheric pressure. Figure 8 was constructed by combining the data of Figure 7 with the known heat content of the same naphtha vapors (naphtha C), at various temperatures and atmospheric pressure.

The dotted curve at the lower left of Figure 8 is intended to enclose the region in which a two-phase system can exist. The critical temperature is shown as 575° F., and the critical pressure as 500 pounds per square inch gage. The choice of the critical conditions is supported by the fact, apparent from Figure 7, that the temperature decrease on expansion becomes more or less independent of initial pressure when the initial temperature is between 570–80° F., and the pressure is at some value, not exactly determinable from the curves, but greater than 400 pounds and less than 600 pounds. Though there is admittedly an arbitrary element in the choice of the critical conditions, it is perhaps more important to appreciate that the shape of the phase boundary of Figure 8 is only a guess, which follows orthodox conceptions built around Amagat's and subsequent investigators' work with carbon dioxide and the implications of the simple theory of the continuity of state. However, Callendar's work on steam (*3*) shows how a comparatively simple pure compound may present striking deviations from stereotyped phase diagrams. One can only hope that this work will stimulate study of the interesting but neglected field relating to the critical phenomena of complex mixtures.

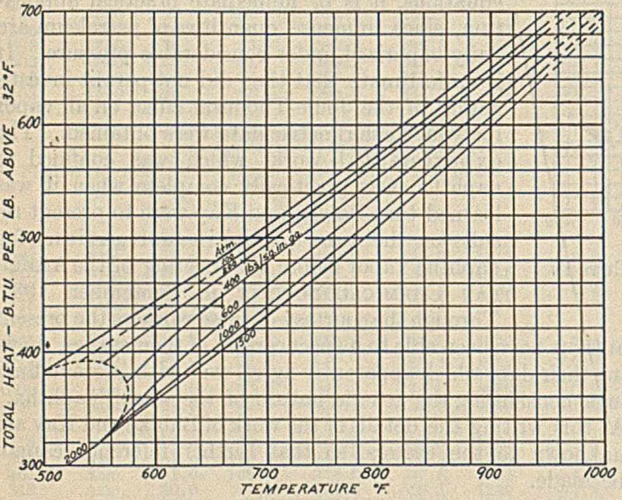

FIGURE 8. EFFECT OF PRESSURE ON TOTAL HEAT OF 58° A. P. I. NAPHTHA VAPOR

McKee and Parker (*7*) and Watson (*9*) have suggested methods for calculating the critical temperature of petroleum mixtures based on their observation of the disappearance of a meniscus in closed capillaries. Table III sets forth the results of calculation by the two methods applied to all oils studied in the work. It will be noted that the above-mentioned critical temperature of naphtha, 575° F., obtained in a different way, happens to be the exact mean of the two tabular values.

TABLE III. CRITICAL TEMPERATURE CALCULATIONS

	MCKEE AND PARKER (*7*)	WATSON (*9*)
	° *F.*	° *F.*
Naphtha (sample C), 58° A. P. I.	560	590
Refined oil, 41° A. P. I.	740	760
Gas oil (sample A), 35° A. P. I.	910	950
Lubricating oil, 20° A. P. I.	1110	1020
Gas oil (sample B), 15° A. P. I.	810	..
	900[a]	..

[a] Calculated using constant recommended for aromatic compounds.

Actual determinations of the critical temperature by a closed-tube method, similar to that used by McKee and Parker (*7*), yielded the results shown in Table IV. The apparatus was designed to permit mixing of the contents of the tubes by inverting them repeatedly just before the critical phenomena were observed.

Table IV shows the results obtained on two naphthas and the refractory gas oil B. The data reported for pure benzene indicate that the determinations are 4° to 5° F. high. It is therefore suggested that the critical temperature of naphtha C is 585° F. No doubt this value is more nearly correct than the estimate of 575° F. from the heat data, but the shape of the two-phase boundary on Figure 8 is not significantly altered by this fact.

TABLE IV. DETERMINATIONS OF CRITICAL TEMPERATURES

METHOD OF FILLING TUBE	OBSERVED CRITICAL TEMPERATURES[a]			
	Naphtha C	Naphtha B	Gas oil B	Benzene[b]
Sealed while still containing air	590	592	.....	556
	590	595		
Sealed while evacuated, keeping part of tube containing liquid in CO_2 snow	590	596	907–912	557
	590	594		
Air driven out by evaporation of part of tube contents:				
10% vaporized	605	605	.....	...
20% vaporized	610	608	.....	...

[a] In all cases except gas oil B, each value of the critical temperature represents some 10 to 15 determinations with the same tube, for which the critical temperature never varied more than 2° F. In the case of gas oil B, the critical temperature changed due to cracking.

[b] Benzene sample was C. P.; melting point, 5.35° C. Critical temperature of pure benzene is given in International Critical Tables as 551.5° F.

EXPERIMENTAL EQUIPMENT AND METHOD

A dual purpose colored the development of both equipment and method for obtaining the heat-content data presented above. Not only was it hoped to get reliable heat-content data at high temperatures, but every effort was made to keep the apparatus and manipulation simple enough to use "in the field" to obtain good heat data on flowing streams of unknown hydrocarbons in refinery apparatus. No further reference will be made to this application of the method since its feasibility will be obvious after the description is completed.

Figure 9 diagrams the essential feature of the equipment used to heat the oil continuously, and Figure 10 shows a larger cross-sectional view of the special steel fitting at the outlet of the heater adapted to injection of the hot hydrocarbon stream into the calorimeter shown as *P*.

In Figure 9, the oil whose heat capacity was to be measured was taken continuously from tank *A* by plunger pump *B*, the capacity of which could be adjusted to any one of several rates intermediate between 3 and 16 gallons per hour. The furnace, *C*, consisted of a refractory brick-lined chamber through which passed eighteen Glo-bar electrical-resistance heating elements 12 inches long by $^5/_8$ inch in diameter, the whole capable of dissipating some 35 kw.

These Glo-bars were arranged two in series across a direct-current line, the voltage of which could be varied up to 150 volts. Heating coil *D*, consisting of 30 feet of $^1/_4$-inch extra heavy pipe-size seamless steel tubing, was shaped to fit the furnace. This furnace and accessories had been designed and built for use in unpublished experiments of a different character, but it served very nicely for this work with the following additions. At the outlet of the coil a steel cross, *E*, was placed, one outlet of which led to a pressure gage, *F*. A steel needle valve, *G*, through which some of the oil was vented to a condenser, *H*, was provided for the opposite outlet. This valve was used only in the runs with vapors at atmospheric pressure as a means to vent excess oil. The special fitting, *J*, shown in Figure 10 was connected to the third outlet of the cross. The major portion of the oil passed at all times through this fitting, *J*, which was arranged so that the thermocouple, *K*, read the temperature at the point where the needle valve stem was seated. There was no dead pocket in which oil could be trapped even momentarily on its way out to condenser *H* through steel valve *L*. Just below the seat of the needle valve in the special fitting, *J*, a $1^1/_2$ inch length of $^1/_8$-inch pipe, *N*, threaded at the lower end was welded. This served as the outlet for oil to the calorimeter.

Before making a determination, a cool, dry, empty, vacuum-jacketed bottle was first weighed. The bottle was then filled with crushed ice (made from distilled water) which had previously been cooled to some temperature well below 32° F. (0° C.). After thorough shaking and mixing, a thermometer which could be read to 0.5° F. was used to take the temperature at several points in the mass of crushed ice, and an average taken. The maximum difference in temperature between various points in the bottle was never greater than 2° F. Supercooling of the ice was necessary to prevent the presence of a thin film of water on the ice particles. The results of the few experiments where an average temperature greater than 30° F. was recorded (see Table II) should be given less weight than the other experiments. After the ice temperature was obtained, the thermometer was withdrawn, and the bottle corked and carefully weighed. The $9^1/_2$ inch length of $^1/_8$-inch pipe and concentric jacket assembly, shown as *M* in Figure 10, whose weight and temperature were known, was then quickly attached to the pipe fitting at the base draw-off valve, *J*. The bottle containing ice was carefully raised up and over this pipe, and the needle valve opened to allow oil to pass into the bottle at as rapid a rate as possible. Temperatures of the oil shown by thermocouple *K* were recorded in rapid succession during the period that oil was being introduced into the bottle calorimeter. The pressure on the oil stream shown by gage *F* was held constant during the run. As soon as all the ice was melted, taking from 1 to 4 minutes, the needle valve was closed, the pipe assembly, *M*, quickly uncoupled and lowered into the bottle which was immediately corked and weighed. After thorough mixing, the cork was removed, and the temperature of the water and oil mixture was taken by a thermometer.

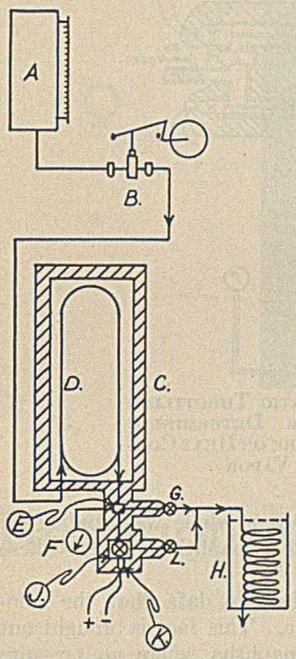

FIGURE 9. FURNACE AND ACCESSORIES FOR DETERMINATION OF TOTAL HEAT OF OIL

EXAMINATION OF EXPERIMENTAL ACCURACY

The following factors entering into the calculations, or bearing upon the accuracy of a determination, were examined quantitatively by more or less conventional methods. The average of the data accumulated for any factor is given directly after its listing:

1. Heat transfer from or to calorimeter during a run, less than 0.05 B. t. u. (12.6 cal.) in all cases.
2. Heat equivalent of calorimeter, 0.0802 B. t. u. per ° F. (36.4 cal. per ° C.).
3. Heat equivalent of pipe and coupling for introducing hot-oil stream; two pipes used—one 0.0298 B. t. u. per ° F. (13.5 cal. per ° C.), the other 0.0571 B. t. u. per ° F. (25.9 cal. per ° C.).
4. Accuracy of pressure gages, thermometers, thermocouples, potentiometer, balance, etc., were all tested, but the integrity of these factors is most clearly shown by steam data to be mentioned.

The difficulties inherent to determining high temperatures accurately, particularly if the material being investigated is a gas, has been the subject of much discussion in the literature. Had it not been for the fortunate fact that the accuracy of the high-temperature measuring devices and of the extra calorimetric equipment could be checked by determining the total heat of steam and comparing it with the accepted data on this material, the task of proving the present method sound would have been much more difficult.

As it was, data plotted as points in Figure 11 (see Table II) were obtained for steam, using the same general method as for the oils and applying the same corrections. Marks and Davis (*6*) give data corresponding to the solid line. The average deviation of present data from the line is +1.3 per cent, the maximum deviation being +3.4 per cent. This agreement was considered satisfactory since one of the principal factors which necessarily influenced design and operation of this equipment was the possibility of cracking the oils. Adjuncts which might have increased the apparent accuracy of the determinations were not applied on account of this fact, and it was gratifying to obtain such checks on the heat content of steam for which data of very high order of accuracy exist.

It is clear, however, that the determination of the heat content of steam does not involve one possible source of considerable error in measuring the heat content of a liquid by apparatus such as that diagrammatically illustrated in Figure 10. On releasing a liquid from high pressure, and temperature above the vaporization point, to atmospheric pressure by the opening of the needle valve, *J*, a large amount of vaporization could be expected to occur in the conduit, *N*. This vaporization would cause instantaneous cooling of the stream when released. The channel, *N*, in the steel block valve, *J*, did indeed transfer a considerable amount of heat to the cooled stream in the runs with naphtha. It was thus necessary to subtract a correction term from each determined value of the total heat in those runs with naphtha in the liquid phase. These corrected values are shown in Table II.

The magnitude of the correction term was obtained by the following argument. It seemed reasonable to assume that Equation 1, found to hold for refined oil, gas oil, and lubricating oil, should also hold for the naphtha. As a matter of fact, uncorrected naphtha data at 200° F., where little flash vaporization could occur, did agree well with the equation. The deviation appeared at higher temperatures. It was known that at 400° F., or above, the naphtha could exist only as a vapor at atmospheric pressure. Since the latent heat of vaporization was known approximately, the temperature differential between the valve block, *J*, and the naphtha, instantaneously and completely flashed to vapor, could be calculated. The heat-transfer coefficient between pipe and vapor, necessary to account for the difference between the uncorrected liquid-heat content and the (assumed) correct value determined from Equation 1, could then be calculated above 400° F.

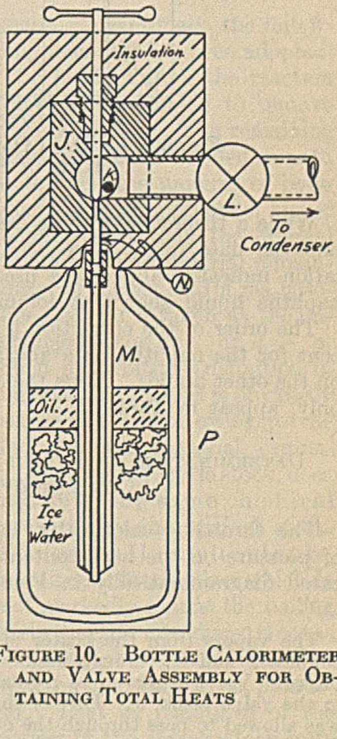

FIGURE 10. BOTTLE CALORIMETER AND VALVE ASSEMBLY FOR OBTAINING TOTAL HEATS

By applying Piroomov and Beiswenger's method (*8*) of calculating the percentage of vaporization *vs.* temperature relationship for a given petroleum fraction, the necessary data for calculating such heat-transfer coefficients down to 250° F. was at hand. On actually carrying out such calculations the results were as follows:

Liquid Temperature before Release of Pressure	Calculated Heat-Transfer Coefficient, Metal Surface to Vaporizing Naphtha
° F.	*B. t. u./hour/sq. ft./° F.*
500	100
450	107
400	121
350	127
300	121
250	122

The rough constancy of these values was deemed strong evidence that the magnitude of the correction term could be calculated by this method, and conversely that the deviation of the naphtha data from general Equation 1 was due to this fact of vaporization and abstraction of heat by the naphtha passing through conduit *N*.

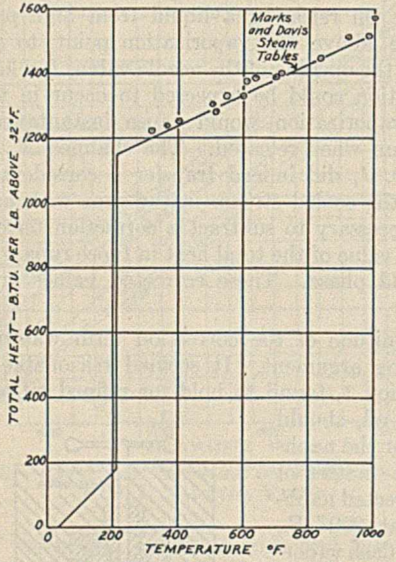

FIGURE 11. DATA OBTAINED ON TOTAL HEAT OF STEAM

While a theoretically more exact means of correcting the naphtha data might have been applied, the simple calculation indicated above was used to obtain the figures for naphtha liquid shown as column 8, Table II.

The order of the correction term is not more than 10 per cent for the naphtha data and is negligibly small for data on the other liquids. Thus the corrected values, for naphtha only, appear in Table II.

DETERMINATION OF EFFECT OF PRESSURE ON HEAT CONTENT OF VAPORS

The throttling calorimeter, used to determine the effect of pressure on the heat content of naphtha vapor, is indicated diagrammatically in Figure 12.

The vapors from the heater of Figure 9 pass over thermocouples *Y* and *K*, through needle valve *L*, and out to the condenser. Valve *L* served to regulate the pressure on the vapor in the valve block, *J*. Part of the oil flowing through valve *J* was allowed to pass through the outlet, *N*, into the calorimeter, *S*. The course of the vapor, after expansion into *S*, was through a layer of steel wool, *R-R*, thence downward over thermocouple *T*, through ports *V*, up through annular jacket *W*, and out to the condenser over thermocouple *X*. The pressure in the atmospheric chamber, *S*, was never more than a few inches of water above atmospheric pressure, as indicated by the pressure gage shown. The pressure before expansion was read from a gage not shown in Figure 12.

Before taking readings, calorimeter conditions remained constant for many minutes, after which a number of pressure and temperature readings were recorded for the various positions in the apparatus. These data have been summarized and appear on Figure 7, and in Table II.

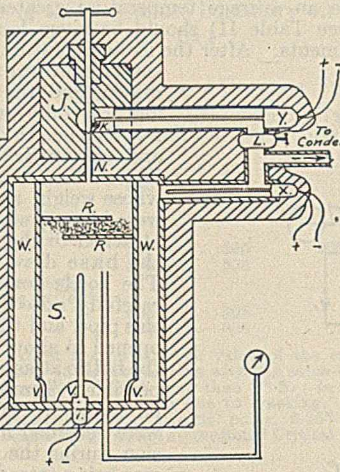

FIGURE 12. ADIABATIC THROTTLING CALORIMETER FOR DETERMINING EFFECT OF PRESSURE ON HEAT CONTENT OF NAPHTHA VAPOR

The accuracy of the method as a whole was studied by making runs with steam instead of naphtha vapor. These data also appear in Table II.

It is apparent upon study of these data that the calorimeter was very nearly adiabatic. This fact is brought out also in the data reported for naphtha where no pressure drop occurred from block *J* to calorimeter *S*.

ACKNOWLEDGMENT

The writers wish to acknowledge their indebtedness to C. A. Porter and F. I. L. Lawrence of The Atlantic Refining Company for their assistance in carrying out the experimental work and for the many suggestions made in the course of this work.

Acknowledgment is also due other members of the Process Division, who aided in obtaining analytical data, and whose criticism was very helpful.

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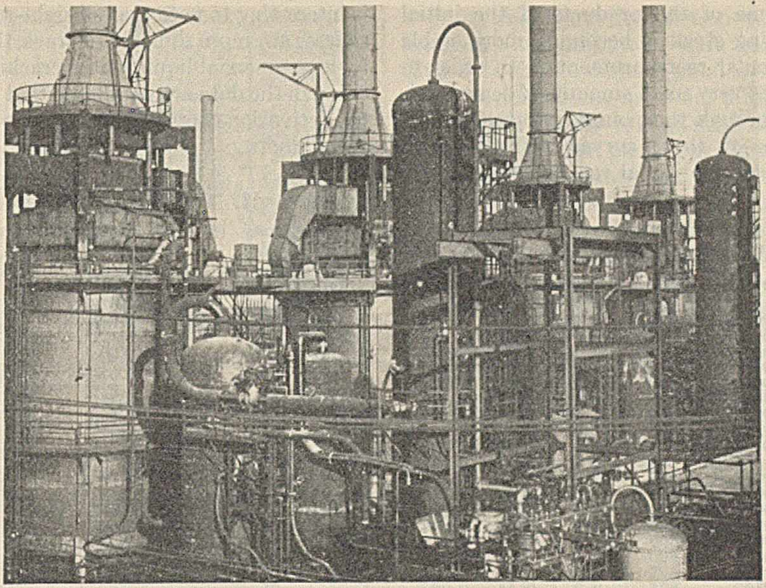
RECEIVED October 26, 1931.

CORRECTION. In the paper entitled "1931 Passes in Chemical Review" [IND. ENG. CHEM., 24, 6 (1932)], the second item in the synthesis of Duprene should be monovinylacetylene instead of monovinylacetate.

On page 9 of the same article, the name of the new honorary fraternity, founded at the University of Illinois, should be Omega Chi Epsilon instead of Theta Chi Epsilon; it should be added that this is strictly a chemical engineering organization, as chemistry students are not admitted to membership.



De Florez Cracking Plant, Philadelphia Refinery of Atlantic Refining Co.

Reaction-Velocity Constants of Oil Cracking

J. C. Geniesse and Raymond Reuter, *The Atlantic Refining Co., Philadelphia, Pa.*

ATMOSPHERIC-PRESSURE data on the cracking of a Midcontinent-type gas oil have been examined with the aid of the monomolecular-reaction equation. Reaction velocity constants, representing the rate of production of materials boiling above and below the distillation range of the original charge, vary with temperature according to the equation:

$$k = 28.8e^{-53,400/RT}$$

Similar calculations on data from the decomposition of straight-run naphthas and pressure-cracked distillates give lines parallel to that for gas oil when plotted on the chart for log k. vs. 1/T. A comparison of these petroleum fractions with the literature data for the pure hydrocarbons shows that practically all of them fall on parallel lines, indicating approximately the same activation energy per gram mole decomposed.

IN VIEW of the increasing interest in the decomposition reaction velocities of the light hydrocarbons, it was thought that similar calculations for the cracking of a heavy petroleum-oil fraction would prove very interesting. Accordingly, the data on the cracking of oil previously presented by the authors (*3*) were studied to see how the reaction velocities compared with those for the light hydrocarbons.

The data on the cracking of pure hydrocarbons have shown that the reaction is probably monomolecular, and that, therefore, the reaction velocity, k, could be calculated most accurately by the use of the monomolecular equation:

$$k = \frac{1}{t} \log_e \frac{a}{a - x}$$

where a = initial quantity of hydrocarbon, and $a - x$ = quantity remaining at time t

In the case of the pure hydrocarbon the calculation is relatively simple since the quantity of undecomposed material can be determined. Careful fractionation and absorption processes make the estimation quite possible. However, in the case of the heavy petroleum fraction such an analysis cannot be made because present knowledge of the properties of the heavier hydrocarbons which enter into the reaction is very limited. It becomes necessary in such a case to make some approximations, if calculations of reaction velocities are to be made. Accordingly, the following procedure has been adopted: The product from the reaction tube is fractionated to remove the gasoline. The remaining material is then distilled so as to determine the amount of polymerization to products of higher boiling point than the original fraction. The material remaining after the removal of gas, gasoline, and tar is taken as the unchanged product, or $a - x$. Such an arbitrary definition of unchanged product is obviously somewhat in error owing to the fact that this material, ordinarily known as recycle stock, does not have the same chemical properties as the original stock. Undoubtedly molecular rearrangements take place which do not markedly change the boiling point of the fraction. Fortunately the error introduced is not as serious as one would first believe, since it has been found that the properties of the recycle were the same for a given production of gas, gasoline, and tar. That is, regardless of the temperature chosen, the properties of the recycle stock were the same if equal amounts of cracking had taken place. Thus, although the calculated reaction velocity would be somewhat in error, the effect of temperature would still be correct.

The oil data for the experiments previously described by the authors (*3*) are given in Table I. In view of the variation of k with amount of cracking, the data were plotted in Figure 1 against $(a - x)$ as abscissa. It may be seen that the reaction velocity decreases as the amount of decomposition increases. This is due to two factors: recycle stock is being produced by the polymerization of some of the products of the initial reactions; and the cracking stock is becoming more stable thermally, owing to molecular rearrangements. In order to estimate the reaction rate at very small amounts of decomposition, curves were drawn through the points as shown in the figure. The intersections of these curves with the zero decomposition line represent the initial reaction rates at the temperatures indicated.

TABLE I. REACTION VELOCITIES OF LISBON GAS OIL

TEMP. ° C.	TIME *Seconds*	$(a - x)$	k(sec.)
430	1100	0.90	0.000095
430	4800	0.70	0.00010
460	942	0.73	0.00033
460	4030	0.39	0.00022
500	5.9	0.96	0.0066
500	13.5	0.95	0.0036
500	26.9	0.91	0.0035
500	27.0	0.89	0.0042
500	62.8	0.79	0.0038
500	65.4	0.79	0.0037
500	390	0.52	0.0017
500	702	0.35	0.0015
500	738	0.34	0.0015
500	1680	0.25	0.00079
500	3200	0.17	0.00052
550	2.05	0.95	0.024
550	6.0	0.87	0.023
550	7.7	0.86	0.019
550	21.0	0.71	0.016
550	436	0.13	0.0043
550	481	0.13	0.0038
550	1130	0.10	0.0018
550	2740	0.10	0.00074
580	2.7	0.81	0.077
580	2.7	0.79	0.088
580	2.8	0.80	0.082
580	2.83	0.83	0.066
580	14.7	0.68	0.026
580	10.1	0.55	0.059
580	10.5	0.61	0.047
580	11.0	0.53	0.058
580	21.3	0.43	0.040
580	28.4	0.31	0.041
580	28.7	0.34	0.048
600	0.80	0.89	0.14
600	1.13	0.84	0.15
600	3.05	0.72	0.11
600	3.0	0.67	0.13
600	3.7	0.69	0.10
600	6.4	0.48	0.11
600	6.4	0.49	0.11
600	7.4	0.41	0.12
600	7.5	0.49	0.095
600	8.36	0.47	0.091
600	8.7	0.47	0.087
600	11.5	0.44	0.071
600	11.8	0.38	0.082
600	12.3	0.38	0.079
600	16	0.29	0.078
600	16.4	0.34	0.066
625	1.2	0.69	0.31
625	2.2	0.54	0.28
625	2.7	0.47	0.28
625	2.7	0.50	0.26
625	6.1	0.28	0.21
640	0.75	0.69	0.49
640	1.3	0.61	0.38
640	2.23	0.38	0.43
640	2.6	0.38	0.37
640	3.06	0.42	0.28
640	3.08	0.42	0.28
640	3.1	0.34	0.35
640	3.8	0.30	0.32
640	4.76	0.31	0.25
640	9.3	0.17	0.19
640	23.4	0.10	0.098
660	5.1	0.23	0.29
700	1.38	0.09	1.73
700	3.36	0.08	0.75
700	3.9	0.14	0.51

The effect of temperature on the rate of reaction may be predicted from the Marcelin and Rice equation:

$$\log k = \frac{-E}{RT} + C$$

where E = energy of activation
T = absolute temperature
R = gas-law constant
C = a constant

The data were plotted, according to this equation, as shown in Figure 2. The points for zero decomposition, as found in Figure 1, are represented on Figure 2 by the line labeled "gas oil," the equation of which is $k = 28.8e^{-53,400/RT}$. The activation energy, E, is 53,400 calories per gram mole. The temperature increase required for the doubling of the reaction varies from 14° C. at 450° C. to 21° at 600°. Since the oil used in the experiments was taken from Lisbon crude, the data show what may be expected from a representative Midcontinent-type crude. Other crudes would be expected to give straight lines parallel to this one and either above or below it, depending on whether they cracked more easily or with greater difficulty.

NAPHTHAS

Atmospheric-pressure reaction-velocity data for naphthas from various crudes and for cracked distillates are listed in Table II. In this case the method of calculation was similar to that used with the gas oil. The quantity $(a - x)$ was taken as the material remaining after the gas and heavy polymers had been removed. The data have been plotted in Figure 2 for comparison with the gas-oil data. Each point represents the average of all the experiments at the indicated temperature, in case more than one experiment was made. It is interesting to note that straight-run naphthas, regardless of source, are more difficult to crack than the distillates formed by a commercial liquid-phase cracking process. Lines drawn through the data are parallel to that for gas oil, indicating that the activation energy per gram mole is the same for both types of products.

TABLE II. NAPHTHA-CRACKING REACTION VELOCITIES

TEMP. ° C.	TIME *Seconds*	$(a - x)$	k(sec.)
HAYNESVILLE CRUDE NAPHTHA			
580	3	0.96	0.013
580	6	0.92	0.013
580	6	0.91	0.016
640	2	0.71	0.171
PANHANDLE CRUDE NAPHTHA			
580	3	0.95	0.017
580	6	0.91	0.016
580	11	0.86	0.014
600	3	0.89	0.039
625	6	0.64	0.074
PECOS CRUDE NAPHTHA			
600	2.9	0.90	0.034
PENNSYLVANIA CRUDE NAPHTHA			
600	3	0.88	0.047
600	5	0.80	0.045
600	16	0.62	0.030
RANGER CRUDE NAPHTHA			
580	11	0.87	0.013
600	3	0.90	0.035
SEMINOLE CRUDE NAPHTHA			
600	3	0.92	0.028
600	5	0.84	0.035
SPINDLETOP CRUDE NAPHTHA			
600	3.0	0.93	0.027
CRACKED DISTILLATE A			
580	3	0.89	0.038
580	5	0.85	0.032
580	5	0.85	0.032
580	5	0.87	0.028
630	2	0.69	0.187
640	1	0.69	0.374
CRACKED DISTILLATE B			
550	11	0.91	0.0086
580	3	0.91	0.032
580	5	0.82	0.040
600	3	0.81	0.071
600	6	0.74	0.050
625	6	0.57	0.094

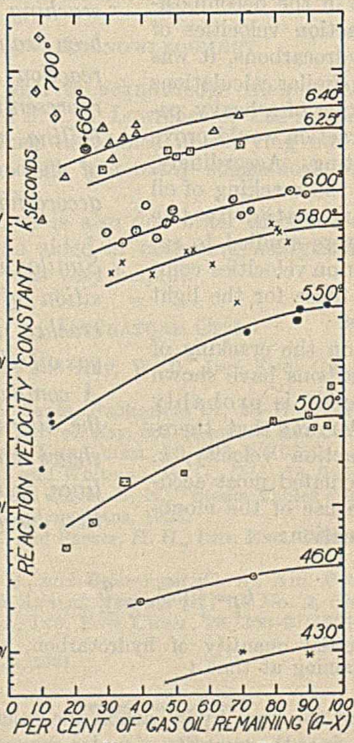


FIGURE 1. VARIATION OF REACTION VELOCITY CONSTANT WITH PERCENTAGE DECOMPOSITION

SATURATED HYDROCARBONS. In order that the data on the petroleum fractions might be compared with the pure hydrocarbons, the reaction velocity constants of the latter have been plotted on Figures 2 and 3. In cases where the amount of decomposition was over 75 per cent, the data have not been included in the comparison since, under such conditions, secondary reactions would considerably affect the results. Bone and Coward's recalculated data (*1*) for methane, shown in Table III, indicate a considerable trend with the amount of cracking. On Figure 2 a line has been drawn through the points at 785° and 985° C. since both of those experiments have approximately the same amount of decomposition.

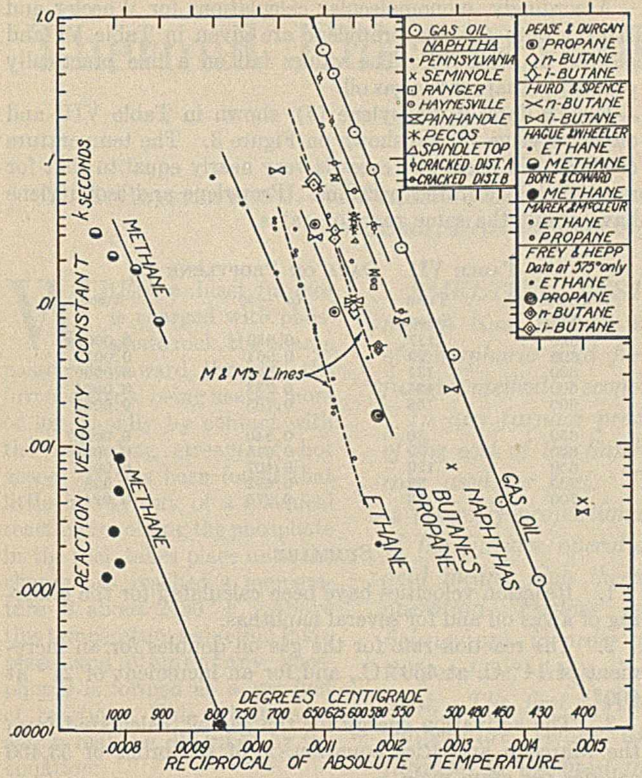


Figure 2. Variation of Reaction Velocity Constant with Temperature

This line is also parallel to the petroleum-fraction lines indicating the same activation energy per gram mole.

Table III. Data for Methane (*1*)

Temp. ° C.	Time Seconds	$(a - x)$	k(sec.)
785	3600	0.96	0.000011
985	60	0.95	0.00082
985	300	0.86	0.00048
1000	900	0.80	0.00025
985	1800	0.77	0.00015
1015	3600	0.65	0.00012

Calculated velocities from Hague and Wheeler's data (*4*) on methane and ethane, listed in Table IV, include only one experiment at each temperature; therefore the variation in the reaction velocity constant is due to both effects—temperature and amount of cracking. The points as shown in Figure 2 are consistent with lines drawn parallel with those for the petroleum fractions. However, the data for methane are entirely different from those of Bone and Coward. Undoubtedly a large part of this difference is due to the questionable practice of measuring the temperature of stream experiments with a single thermocouple. Thermocouples need to be placed at various points along the tube if uniform temperature is desired.

Table IV. Data on Methane and Ethane (*4*)

(Gas feed, 4 liters per hour at room temperature; volume of reaction zone 114.2 cc.)

Gas Flow at Cracking Temp. Cc. per sec.	Temp. ° C.	Time Seconds	$(a - x)$	k(sec.)
		METHANE		
4.42	900	25.9	0.83	0.0074
4.69	950	24.4	0.66	0.017
5.20	1000	22.0	0.63	0.021
5.66	1050	20.2	0.55	0.030
		ETHANE		
4.25	700	26.9	0.66	0.016
5.07	750	22.5	0.34	0.048
5.33	800	21.5	0.21	0.073

Pease and Durgen's reaction velocities (*10*) for propane, *n*-butane, and isobutane were calculated by them. Since their data show a definite trend with amount of cracking, the points corresponding to zero or initial cracking were estimated in a manner similar to that used in Figure 1. The points so obtained have been plotted in Figure 2. Both butanes crack at about the same rate, and the temperature effect is parallel to that for the petroleum fractions. Only two points are given for propane. They are consistent with the other data. It may be seen that propane decomposes more slowly than the butanes, which in turn are more stable than the naphthas.

Hurd and Spence's data (*6*) on *n*-butane and isobutane, as recalculated and presented in Table V, do not fall on a line parallel to the others when plotted in Figure 2. The reason for the deviation is not obvious. Perhaps part of it may be due to the very small amount of decomposition at 400° C. Nevertheless the data show that both of the butanes decompose at the same rate, and that at 600° C. the rate is the same as Pease's for the same hydrocarbons.

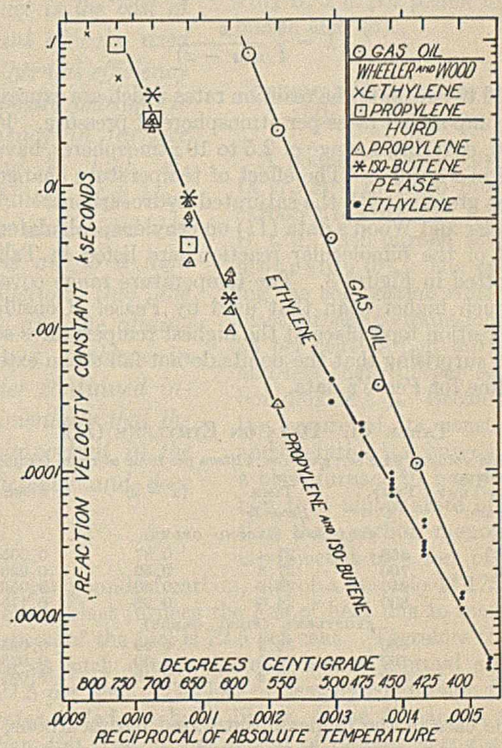


Figure 3. Variation of Reaction Velocity Constant with Temperature

Table V. Data on *n*-Butane and Isobutane (*6*)

Temp. ° C.	Time Seconds	$(a - x)$	k(sec.)	Temp. ° C.	Time Seconds	$(a - x)$	k(sec.)
n-BUTANE				ISOBUTANE			
400	31	0.987	0.00042	400	30	0.989	0.00033
500	27	0.981	0.00070	500	27	0.926	0.0028
600	19	0.79	0.013	500	8	0.985	0.002
600	19	0.76	0.015	550	8	0.946	0.007
600	22	0.84	0.0079	550	10	0.925	0.0077
600	30	0.78	0.0082	600	9	0.89	0.013
600	24	0.80	0.0093	600	17	0.87	0.0082
				600	21	0.81	0.0099
				600	26	0.75	0.011
				600	27	0.78	0.0091
				650	7	0.81	0.029
				700	6	0.61	0.083

Marek and McCluer (*8*) have studied the decomposition of ethane and propane. Their data are plotted in Figure 2. Their percentage decomposition for ethane at 600° C. (0.6 per cent) is very small. A slight error here could move the point enough to bring a line through the data parallel to the others in Figure 2 although displaced from Hague and Wheeler's data. Similar comment is true of their line for propane.

Frey and Hepp (*2*) give velocity constants for eight of the simpler paraffins at 575° C. Their data are plotted in Figure 2 where it may be seen that the value for ethane falls on the extrapolated lines of either Hague and Wheeler or Marek and McCluer. Their value for propane falls in line with Pease's data, and their values for normal and isobutane are in accordance with the line which has been drawn through the data of both Pease and Hurd.

Thus the present writers' data on a gas oil and on various naphthas, together with the work of six independent authors on pure hydrocarbons, are suitably expressed by a family of parallel lines in Figure 2.

UNSATURATED HYDROCARBONS. An examination of the ethylene data shows that the main reaction is one of polymerization. Therefore, the bimolecular equation,

$$k = \frac{1}{t}\,\frac{x}{a(a - x)}$$

was used to calculate the reaction rates which are expressed as the decomposition rates per atmosphere of pressure. Pease's data (*9*), covering a range of 2.5 to 10 atmospheres, have been plotted in Figure 3. The effect of temperature change on k is not as great as with the saturated hydrocarbons.

Wheeler and Wood's data (*11*) on ethylene, calculated with the aid of the bimolecular reaction, are listed in Table VI and plotted in Figure 3. The temperature range covered is very much higher than that used by Pease. Considerable decomposition took place at the highest temperatures so that it is not surprising that the points do not fall on an extension of the line for Pease's data.

TABLE VI. DATA ON ETHYLENE (*11*)

(Apparatus volume, 94.2 cc.; gas flow, 4 liters per hour at room temperature)

GAS FLOW AT CRACKING TEMP. *Cc. per sec.*	TEMP. ° *C.*	TIME *Seconds*	$(a - x)$	k(sec.)
		ETHYLENE (SECOND ORDER)		
3.43	650	27.4	0.87	0.0055
3.38	700	27.8	0.56	0.028
3.54	750	26.6	0.40	0.056
3.82	800	24.6	0.26	0.116
		PROPYLENE (FIRST ORDER)		
3.51	650	26.9	0.90	0.0039
3.85	700	24.5	0.50	0.028
4.25	750	22.2	0.12	0.098

In the case of the higher unsaturated hydrocarbons, there are no data at pressures higher than one atmosphere; therefore it was impossible to determine whether the reactions are monomolecular or bimolecular. Calculations based on either equation would give almost the same results, owing to the fact that all experiments were made at one pressure. Inasmuch as the ratio of decomposed to polymerized material increased decidedly with increase of the size of the unsaturated molecule, it was thought advisable to use the monomolecular equation for the propylenes and butylenes rather than the bimolecular equation.

Accordingly, monomolecular calculations for Wheeler and Wood's data (*11*) on propylene are given in Table VI and plotted in Figure 3. The values fall on a line practically parallel to that for the gas oil.

Hurd's data on propylene (*5*), shown in Table VII, and on isobutylene (*7*) are shown on Figure 3. The temperature coefficient in these two cases is very nearly equal to that for most of the saturated paraffins. Propylene and isobutylene have about the same reaction rates.

TABLE VII. DATA ON PROPYLENE (5)

TEMP. ° *C.*	TIME *Seconds*	$(a - x)$	k(sec.)
550	137	0.959	0.00029
600	29	0.961	0.0013
600	131	0.845	0.00097
600	125	0.733	0.0024
600	158	0.703	0.0022
650	30	0.840	0.00287
650	79	0.616	0.0061
650	120	0.407	0.0075
700	25	0.492	0.028
700	53	0.275	0.024

SUMMARY

1. Reaction velocities have been calculated for the cracking of a gas oil and for several naphthas.
2. The reaction rate for the gas oil doubles for an increment of 14° C. at 450° C., and for an increment of 21° at 600°.
3. The activation energy for the gas oil, calculated from the Marcelin and Rice equation, is of the order of 53,400 calories per gram mole.
4. Pressure-cracked naphthas crack more easily than straight-run crude naphthas. Both types of material require the same activation energy as gas oil.
5. Comparison of petroleum fractions with pure light hydrocarbons show the rates of decomposition to increase as the molecular weight increases.
6. With the exception of ethylene, which polymerizes when heated, the group of lines with equal slopes shows that the activation energies for decomposition of all the hydrocarbons and petroleum fractions are the same.

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RECEIVED October 17, 1931. Presented before the Division of Petroleum Chemistry at the 82nd Meeting of the American Chemical Society, Buffalo, N. Y., August 31 to September 4, 1931.

ZINC IN 1931. Unfavorable industrial conditions throughout the world continued to affect the United States zinc industry in 1931, according to the Bureau of Mines. The year witnessed the lowest production since 1921.

The output of primary metallic zinc from domestic ores was 40 per cent lower than in 1930, following a decline of 20 per cent in output in 1930. Apparent deliveries of primary zinc to consumers were 21 per cent below those of 1930 which, in turn, were 28 per cent below those of 1929. As evidence that zinc producers were attempting to meet existing conditions, smelter stocks were reduced from 167,293 tons at the end of 1930 to 135,600 tons at the end of 1931, a drop of 19 per cent. This reduction is noteworthy, for it was achieved in spite of a large decrease in consumption.

The output of primary metallic zinc from domestic ores in 1931, as reported by producers from figures of actual production for eleven months and estimates for December, was about 292,000 tons and no output was reported from foreign ores. In 1930, 489,361 tons were produced from domestic ores and 8684 tons from foreign ores, or a total of 498,045 tons. The decrease in total primary production for 1931 as compared with 1930 amounted to 41 per cent. In addition to the output of primary zinc, about 21,000 tons of redistilled secondary zinc were produced, as compared with 34,849 tons in 1930.

Thermal Efficiency of the Phosphate Blast Furnace

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SMELTING TESTS with a small experimental blast furnace show that the production of phosphoric acid for fertilizers by the blast-furnace method is economically practicable.

In any furnace process more than two-thirds of the cost of the finished product is the cost of coke used for fuel. The amount of coke used is inversely proportional to the thermal efficiency of the furnace operation. Low-cost phosphoric acid means high thermal efficiency in furnace operation. Factors contributing to high efficiency are, in order of importance: high blast temperature; large-size furnace unit; and dry blast. The first (preheating the air to a high temperature before its introduction into the furnace) is the most important, and the attainment of maximum preheat is a problem in equipment design which is under continued investigation. It is shown experimentally that the grade of phosphate rock is unimportant in the realization of high thermal efficiency and does not influence coke consumption.

When a blast furnace is charged with phosphate rock, the charge passes downward through the furnace shaft, being heated more or less rapidly by contact with the ascending stream of hot gases. It has been found that little in the way of a chemical reaction involving the phosphate in the rock takes place until the charge has reached a temperature of about 2430° F. Above this temperature reduction takes place, and elementary phosphorus is formed as a product of reaction. This reduction reaction may be described by the equation:

$$Ca_3P_2O_8 + 5C = 3CaO + P_2 + 5CO \quad (1)$$

Equation 1 seems to imply that a chemical reaction takes place between two solids. Obviously this is not what actually occurs. Two suggestions may be offered to explain the mechanism of reduction. It is possible that, at the temperatures prevailing in the lower part of the blast furnace, tricalcium phosphate may be subject to thermal dissociation:

$$Ca_3P_2O_8 \rightleftharpoons 3CaO + P_2O_5 \quad (2)$$

The phosphoric acid resulting from this dissociation, being a gas and coming in contact with solid carbon, will be reduced according to the equation:

$$P_2O_5 + 5C = P_2 + 5CO \quad (3)$$

The algebraic sum of Equations 2 and 3 is identical with Equation 1. It may also be considered possible that tricalcium phosphate is reduced by the carbon monoxide, that the resulting carbon dioxide reacts with coke, and that carbon monoxide is regenerated. Thus:

$$Ca_3P_2O_8 + 5CO = 3CaO + P_2 + 5CO_2 \quad (4)$$

$$5CO_2 + 5C = 10\ CO \quad (5)$$

As before, the sum of Equations 4 and 5 is identical with Equation 1. Not enough is known of the properties of tricalcium phosphate at high temperatures to choose between the two sets of equations, and the facts may be described for present purposes by Equation 1.

In a phosphate-furnace process it is necessary not only to separate and recover phosphorus as a product, but also to maintain the furnace in continuous operation. It is therefore necessary to remove the lime which appears in the above equations as a product of reaction. Silica and alumina present in low-grade phosphate rock or added as flux to high-grade rock combine with lime to form a fluid slag. The equation:

$$Ca_3P_2O_8 + 5C + 3SiO_2 = 3CaSiO_3 + P_2 + 5CO \quad (6)$$

indicates formally the effect of silica. This reaction is endothermic to the extent of 4151 B. t. u. per pound of phosphoric acid (*3*).

Thermal Efficiency of the Blast Furnace

A pound of carbon generates 14,175 B. t. u. when burned to carbon dioxide (*2*), and 4033 B. t. u. when burned to carbon monoxide (*6*). The gas leaving the combustion zone of the blast furnace contains more than 34 per cent carbon monoxide and less than 0.1 per cent carbon dioxide (*7*). Because from the nature of its construction and operation it is impossible for a blast furnace to burn its carbon to a higher state of oxidation than carbon monoxide, it is subjected to a loss of 10,142 B. t. u. per pound of carbon, out of a possible 14,175; that is, in every blast furnace the loss of heat due to incomplete combustion of the fuel is 72.5 per cent. Therefore the blast furnace as such cannot have a higher thermal efficiency than 27.5 per cent. The loss of heat by conduction through the water-cooled fire-brick lining of the furnace is seldom less than 400 B. t. u. per pound of carbon consumed, and the loss of heat in the conversion of blast moisture into hydrogen (an unavoidable reaction) will average 200 B. t. u. per pound of carbon. The net heat will therefore be 3433 B. t. u. out of 14,175, indicating a furnace efficiency of some 24 per cent.

Although the 10,142 B. t. u. per pound of carbon "loss of heat due to incomplete combustion of fuel" is lost to the furnace, this energy remains in the waste gas emerging from the furnace top as heat of combustion of the gas. In every actual blast-furnace operation some of this waste gas is burned in a set of regenerative stoves, and a part of the waste heat is restored to the furnace in the form of sensible heat of the hot blast. For example, if the blast be preheated to 1400° F. (as in fact it frequently is) the sensible heat will be 2000 B. t. u. per pound of carbon (*8*). The net heat for such a hot blast furnace will be 3433 generated by combustion plus 2000 brought in by the blast, that is 5433 B. t. u., indicating an efficiency of 38 per cent. A study of standard blast-furnace practice, as it has been carried out in the iron and steel industry, leads to the conclusion that it is difficult but not impossible to operate the better types of modern hot-blast stoves as high as 1700° F. The sensible heat of the blast at 1700° F. is 2470 B. t. u. per pound of carbon. In this case the total heat is 5903 B. t. u., and the furnace efficiency just over 41 per cent.

Efficiency of Phosphate Reduction

The heat absorbed by the endothermic reaction indicated by Equation 6 is 4151 B. t. u. per pound of phosphoric acid when and if the reaction is carried out at room temperature. As will be seen later, this reaction actually takes place at about 2430° F. To determine the heat absorbed by the reaction at the higher temperature, it is required to know not only the specific heat of carbon monoxide, carbon, silica, and calcium silicate over the temperature range from room temperature to 2400° F. (thermal quantities which are known well enough), but also the specific heats of tricalcium phosphate and of phosphorus gas, which unfortunately are not known at all. The reaction heat will therefore be assumed to be 4151 B. t. u. at 2400° F. with the understanding that this figure is undoubtedly incorrect.

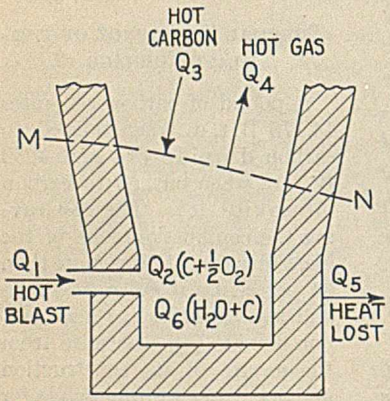

Figure 1. Bosh and Hearth of Phosphate Blast Furnace

The gases leaving the reduction zone in the phosphate blast furnace are at or above 2430° F. The sensible heat of the furnace gases lost in this way to the reduction zone is 4400 B. t. u. per pound of carbon. There is, however, brought into the reduction zone by the carbon which enters already preheated by its descent through the upper part of the furnace, 875 B. t. u. per pound as sensible heat of hot carbon (*4*). The carbon comes into the reduction zone carrying 875 B. t. u. with it, and the hot products of combustion leave the reduction zone carrying away 4400 B. t. u. There is therefore a net loss to the reduction zone of 3525 B. t. u. It will be remembered that the net heat generated by the combustion of carbon is 3433 B. t. u. It is obvious therefore that the heat absorbed in the reduction reaction cannot be supplied by the combustion of carbon. Any heat absorbed by reduction of phosphate must be supplied by the hot blast. There is no obvious reason why all of the sensible heat of the hot blast cannot be thus used in promoting the reduction of phosphoric acid. The evidence which the writers have collected during the operation of the Bureau of Chemistry and Soils experimental blast furnace tends to the conclusion that this is, in fact, true. Stated in other terms, the amount of phosphoric acid which can be reduced in any given phosphate blast-furnace operation depends upon the number of B. t. u. supplied to the reduction zone, and upon this alone. It is implied here that there is always sufficient phosphoric acid present to absorb all of the heat supplied to the reduction zone. The operator may assure himself that the requirement is satisfied by charging more phosphate rock than the furnace can reduce, the excess phosphoric acid leaving the furnace unreduced in the slag. The factor which limits the amount of phosphoric acid that can be reduced in the blast furnace is the amount of heat which is supplied to the reduction zone and absorbed there by the reduction reaction. This is seen to be 100 B. t. u. less than the sensible heat of the hot blast. And formally the efficiency of phosphate reduction is the quotient of the sensible heat of the hot blast, minus 100, divided by 14,175 B. t. u. In the case of 1400° F. hot blast, the blast heat is 2000 B. t. u. per pound of carbon, and the efficiency 13.4 per cent [(2000 − 100) ÷ 14,178]. With a hot blast at 1700° F. the blast heat is 2470, and the efficiency of reduction 16.7 per cent [(2470 − 100) ÷ 14,175]. If the blast were dried before its introduction into the furnace, there would be a further average increase of heat supplied, the reduction zone of 200 B. t. u., making the efficiency of reduction 18.1 per cent [(2470 − 100 + 200) ÷ 13,175].

Heat Balance for the Phosphate-Furnace Reduction Zone

The bosh and hearth of a phosphate blast furnace are shown in Figure 1. Let the surface, *MN*, be drawn across the bosh at the location of the 2432° F. isotherm. The temperature at all points below the surface, *MN*, are equal to or in excess of 2430° F. It is proposed to write down a heat balance for so much of the furnace as lies below the surface, *MN*. For this purpose six heat quantities are defined:

Q_1 = Heat brought in by hot blast
Q_2 = Heat generated by reaction $C + {}^1/_2\,O_2 = CO$
Q_3 = Heat brought in by descending carbon
Q_4 = Heat carried out by ascending furnace gases
Q_5 = Heat carried away by thermal conduction through walls
Q_6 = Heat absorbed by blast moisture by reaction $H_2O + C = H_2 + CO$

The units employed are B. t. u. per minute. If Q_r represents the heat available above the temperature of reduction, then Q_r is given by the equation:

$$Q_r = Q_1 + Q_2 + Q_3 - Q_4 - Q_5 - Q_6 \qquad (7)$$

The heat, Q_r, represents the number of B. t. u. supplied to the reduction zone per minute and absorbed therein by the reduction reaction expressed in Equation 6. The amount of phosphoric acid thermally reducible (in pounds per minute) is obtained by dividing Q_r by 4151. It is assumed by the writers that the pounds of phosphoric acid reduced per minute is equal to the amount thermally reducible. The test of the truth of this assumption is the comparison between the observed reduction of phosphoric acid in the experimental furnace and the amount of phosphoric acid which could be theoretically reduced by the heat supplied to the reduction zone.

Results of Blast-Furnace Experiments

Table I gives the results obtained from eight tests made with an experimental blast furnace. This furnace has already been described (*1*).

> It is 80 inches tall with a 19-inch stock line, a 13.5-inch hearth, a 79° bosh angle, and has a total volume of 12 cubic feet. It is blown through one or both of two tuyères. The wind blown was 40 to 60 cubic feet per minute of air which could be heated in a makeshift iron-pipe stove to a little higher than 1200° F. The temperature of the blast was measured with a calibrated chromel-alumel thermocouple. The amount of air blown was measured with a 0.75-inch rounded brass orifice. The bosh and hearth of the furnace were water-cooled. The amount of cooling water and its temperature were measured. Slag was removed from the hearth at half-hour intervals, and samples taken for analysis. The furnace gases carrying the phosphorus were discharged into the air. The amount of phosphoric acid reduced was calculated from the weight and analysis of the material charged into the furnace top, and the weight and analysis of the slag removed from the hearth.

The furnace unit in these experiments was quite small and suffered from the handicap that the heat lost by conduction was unduly high. The undue prominence of this heat quantity could be decreased only by carrying out the experiments with a larger experimental blast furnace. In a full-scale commercial blast furnace the effect of heat loss is of minor importance.

The operating quantities measured during the tests are re-

Table I. Operating Data for Experimental Phosphate Blast Furnace

		Experiment Number							
		I	II	III	IV	V	VI	VII	VIII
1	Coke charged, lb. per hour	62.9	41.7	41.2	59.9	67.8	71.0	47.0	44.7
2	Phosphate rock, lb. per hour	46.7[a]	23.8[b]	23.5[b]	44.4[a]	50.2[a]	52.7[a]	36.1[b]	37.1[b]
3	Air blown (60° F., 30 in. Hg), cu. ft. per min.	58.5	40.0	39.3	55.0	62.5	64.6	42.0	39.9
4	Blast temperature, ° F.	982	682	729	1133	1190	1219	1110	1245
5	Heat lost by conduction, B. t. u. per min.	666	264	263	666	735	670	260	311
6	Slag produced, lb. per hour	69.3	27.8	26.8	64.0	73.0	74.1	39.3	41.4
7	P_2O_5 in slag, %	6.48	8.10	7.26	4.12	4.72	2.86	2.80	5.58
8	P_2O_5 reduced, %	65.1	70.4	73.8	78.4	75.0	85.4	90.6	80.9
9	P_2O_5 reduced, lb. per min.	0.140	0.0883	0.0912	0.160	0.179	0.207	0.173	0.162
10	Heat used in P_2O_5 reduction, B. t. u. per min.	581	368	380	665	746	860	718	674

[a] Tennessee rock.

[b] Florida rock.

corded in Table I. Both the Florida and Tennessee rocks indicated in item 2 were fluxed with suitable additions of crushed fire brick to form a slag easily removable from the hearth. The composition of the two phosphate rocks is given in Table II. The sulfide and sulfate content of the Tennessee blue rock is perhaps unusual but appeared to have no effect upon the furnace operation. The coke used was an off-grade non-metallurgical coke with 80.1 per cent fixed carbon and about 16 per cent ash. In item 11, Table III, in which the coke consumption is given, the fuel is reduced to an "equivalent coke" with the more usual 87 per cent fixed carbon. The physical and chemical properties of the coke, aside from its fixed carbon content, seem to be of little concern in phosphate smelting.

Table II. Analysis of Phosphate Rock Used in Blast-Furnace Experiments

(Dry basis)

	Florida Rock	Tennessee Rock
	%	%
SiO_2	6.90	8.34
Al_2O_3	2.13	...
Fe_2O_3	1.91	0.17
CaO	46.50	40.41
P_2O_5	31.63	27.56
FeS_2	...	10.18
SO_3	...	3.20

It is obvious that little interest can attach to the results of these experiments, except in so far as it may be possible to use them in predicting what operating results may be expected from a blast-furnace unit of commercial size. And from an economic point of view the phrase "operating results" means primarily "coke consumption," that is, the tons of coke required to reduce a ton of phosphoric acid.

A heat balance for so much of the furnace as will include the zone of phosphate reduction for each of the eight experiments is given in Table III. The first six items give the value of the six thermal quantities (Q_1, Q_2, Q_3, Q_4, Q_5, Q_6) appearing in Equation 7. Item 7 gives the value of Q_r calculated by Equation 7. Item 8 shows the observed value of Q_r and is copied from item 10 of Table I. The difference between the observed and the calculated value of Q_r is shown in item 9 in B. t. u. per minute, and again in item 10, expressed in per cent, with Q_r (calculated) taken as 100 per cent. The mean difference is 7 per cent, and the maximum difference 15. The quantity Q_r is calculated by means of six quantities in such a fashion as to magnify the errors involved.

Effect of Slag on Phosphate Reduction

The phosphate rock used in the experiments recorded in Table I was one of two materials: washed rock from Florida, containing 31.63 per cent phosphoric acid on a dry basis; and blue rock from Tennessee, containing 27.56 per cent phosphoric acid. The Tennessee rock was a donation to the Bureau by the Armour Fertilizer Works. Both rocks were too high in calcium oxide, and too low in silica and alumina to yield a satisfactory blast-furnace slag, and in each case the phosphate rock was accompanied into the furnace with enough crushed fire brick to give a desired lime-alumina-silica composition to the resultant slag. In the case of the Tennessee rock, 100 pounds of phosphate rock with its flux and coke ash produced about 145 pounds of slag. With Florida rock the slag produced was about 110 pounds per 100 pounds of rock. These quantities of slag are about as small as would be normally encountered in practice. It is technically of considerable importance, however, to determine whether with relatively large amounts of slag the thermal efficiency of phosphate reduction will be unfavorably affected. The assumptions made in this paper have not taken into account the amount of inert slag-forming materials accompanying the phosphate through the furnace. In fact, if the mechanism of phosphate reduction as here described is correct, the amount of phosphoric acid reduced in a given furnace operation is not dependent upon the grade of rock used nor on the amount of slag produced. It is understood of course that, if the particular rock used is so highly siliceous that the slag becomes unmanageable, mechanical operation of the furnace may become impossible. If the low-grade rock, however, contains sufficient tricalcium phosphate to produce a workable slag, it will be economically as satisfactory a material as c. p. tricalcium phosphate.

It was felt that the technical importance of this conclusion justified its submission to a particularly severe test. Therefore a run (IX) was made in which an extremely low-grade charge was smelted. This charge was made up of thirty-three parts Florida rock, ten parts crushed fire brick, and fifty-seven parts of normal pig-iron blast-furnace slag. This artificial mixture, containing only 10.55 per cent phosphoric

Table III. Heat-Balance for Bosh and Hearth of Experimental Phosphate Blast Furnace

(Thermal quantities in B. t. u. per minute)

			Experiment Number							
			I	II	III	IV	V	VI	VII	VIII
1	Heat in the blast	(Q_1)	1024	467	496	1130	1341	1423	838	917
2	Reaction $C + {}^1/_2O_2 = CO$	(Q_2)	3027	2059	2023	2835	3220	3333	2165	2062
3	Heat in carbon	(Q_3)	654	447	438	614	697	723	469	449
4	Heat in furnace gases	(Q_4)	3313	2255	2219	3103	3523	3646	2372	2258
5	Heat lost by conduction	(Q_5)	772	306	305	770	853	777	302	361
6	Reaction $H_2O + C = H_2 + CO$	(Q_6)	113	35	34	117	121	125	86	85
	Heat available for P_2O_5 reduction:									
7	Q_r (calcd.)		507	377	399	589	761	931	738	624
8	Q_r (obsvd.)		581	368	380	665	746	870	718	674
9	Difference, B. t. u.		+74	−9	−19	+76	−15	−61	−20	+50
10	Difference, %		+14.6	−2.4	−4.8	+12.9	−2.0	−6.6	−2.7	8.0
11	Coke (87% F. C.), tons per ton P_2O_5 reduced (calcd.)		7.60	7.00	6.56	6.22	5.55	4.77	4.01	4.45
12	Coke, tons per ton P_2O_5 reduced (obsvd.)		6.93	7.24	6.91	5.72	5.80	5.25	4.16	4.23
	Thermal efficiency of reduction:									
13	Calculated, %		4.76	5.10	5.62	5.91	6.50	7.96	9.71	8.60
14	Observed, %		5.45	4.97	5.35	6.67	6.36	7.44	9.43	9.30

acid, is comparable with the lowest grades of run-of-mine phosphate rock occurring in Florida.

The data on the test (run IX) were as follows:

Coke charged, lb. per hour	39.6
Phosphate rock, lb. per hour	23.7
Fire brick and slag, lb. per hour	47.6
Air blown, cu. ft. per min.	37.0
Blast temperature, ° F.	716
Heat lost by conduction, B. t. u. per min.	288
Slag produced, lb. per hour	66.9
P_2O_5 in slag, %	4.35
P_2O_5 recoverable, %	61.2
P_2O_5 reduced per min., lb.	0.0765

The heat available for phosphate reduction is:

	B. t. u.
Q_1, sensible heat in hot blast	467
Q_2, heat of reaction $C + {}^1/{}_2O_2$	1911
Q_3, sensible heat of hot carbon	319
Q_4, sensible heat of hot gases	2047
Q_5, heat lost by conduction	288
Q_6, heat of reaction $H_2O + C$	69
Q_r, heat available for reduction	293

Since 4151 B. t. u. are required to reduce a pound of phosphoric acid, the 293 B. t. u. per minute available for phosphate reduction are sufficient to reduce 0.0707 pound phosphorus pentoxide per minute. The actual observed rate of reduction was 0.0765 pound per minute, or 8 per cent more than is expected from the heat balance. The amount of slag produced was large. Errors in sampling, in analysis, and in determining the weight of the slag could easily cause a 10 per cent probable error. More evidence is required to give a final answer to the problem. It is possible, however, to say that the evidence at hand tends to justify the assumption involved in the smelting theory—namely, that in phosphate reduction the coke consumption is governed solely by the heat required by that reaction, and that the question of how much or how little slag is to be melted has no effect one way or the other.

FACTORS INFLUENCING COKE CONSUMPTION

If the validity of Equation 7 be accepted, it is possible to write down a number of conclusions that are of importance to the phosphate furnace designer and operator. Since the coke consumption is a function of one variable, Q_r, and since the value of Q_r depends upon the six heat quantities, Q_1, Q_2, Q_3, Q_4, Q_5, Q_6, it is those six Q's that are alone of importance. One of them, Q_2 (the second largest), can be left out of consideration immediately because it is a chemical constant—the heat generated by the oxidation of carbon to carbon monoxide. The quantity, Q_6, which is normally rather small can be reduced to insignificance by drying the air before introducing it into the furnace. The heat loss, Q_5, which is quite large in the experimental unit, can be decreased to zero by making the size of the furnace infinite. In actual practice the heat loss becomes less than 10 per cent of Q_r in furnaces burning more than 50 tons of coke per day. A large improvement in thermal efficiency could be made by reducing the magnitude of Q_4, the heat carried out of the phosphate reduction zone by the ascending furnace gases. This may be done by decreasing the nitrogen that normally accompanies the oxygen used to burn the carbon at the tuyères. Since this means adding oxygen to the blast (*5*), the expense of which is considerable at present, and since it also means decreasing the value of Q_1, which in some measure neutralizes the benefit derived from decreasing the value of Q_4, the economy of such a procedure must await the production of cheaper oxygen than is at present available. There remains the quantity, Q_1, the sensible heat brought into the furnace by the hot blast. The problem of heating the blast is a research in itself and is one which promises to yield striking results if its solution can be approached.

CONCLUSIONS

It has been found by experiment with the small-scale blast furnace that the phosphoric acid of phosphate rock is separated from the mineral gangue by reduction to elementary phosphorus which, emerging from the furnace in the gas stream, may be assumed to be removable from the blast-furnace gas, after condensation by electrical precipitation or other means. The natural phosphatic minerals of commercial deposits are suitable for direct smelting, as they occur without preliminary treatment. The lowest grades of siliceous Florida mine-run material require fluxing with some basic mineral—e. g., a partially washed rock or a less siliceous mine-run material. The higher grades of Florida or Tennessee rock require addition of sand or siliceous material as a flux. The cost of the phosphatic charge with its flux as charged into the furnace will in any probable commercial development be a small item in the cost of the product.

The problem of major interest from a metallurgical, and also from the engineering and economic point of view, is the coke consumption, that is, the number of tons of coke required to reduce a ton of phosphoric acid. The first four experiments recorded in Table II (experiments I, II, III, and IV) may arbitrarily be called "low" blast-temperature runs, and the last four experiments (V, VI, VII, VIII) "high" blast-temperature. The average for the first group was 882° F. blast temperature, and the average coke consumption 6.70 tons. For the second group the blast temperature was 1191° F., and the average coke consumption 4.81 tons. The over-all fact that an increase of 309° F. in blast temperature caused a drop of 28 per cent in coke consumption gives a correct impression of the influence of blast temperature on coke consumption. In both groups, of course, the coke consumptions are higher than would be found in the operation of a full-scale furnace because of the abnormally high heat-conduction losses in the small experimental unit, but the relative effect is substantially the same as it would be with a larger furnace. Using $8.25 as the cost of coke delivered to a blast furnace located in Florida, the two coke consumptions, 6.70 and 4.81, can be written $55.25 and $39.75 per ton of phosphoric acid for the cost of coke. The increase of 309° F. in blast temperature results in a saving of $15.50. Really low-cost furnace phosphates will be realized in practice from an elevation in blast temperature. Without a more elaborate means for preheating the blast, the writers have been unable to realize a coke consumption of less than 4 tons of coke per ton of phosphoric acid reduced.

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Lead Chromates

Effect of Hydrogen-Ion Concentration on Color of Lead Chromate Pigments from Lead Nitrate and Lead Acetate

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LEAD CHROMATES were prepared from lead nitrates and lead acetates with sodium and potassium dichromates varying the hydrogen-ion concentration. The acidity was regulated with nitric and acetic acids, and potassium and sodium hydroxides. The potentiometric method of Ernst, Pragoff, and Litkenhous (3) was used with quinhydrone as the indicator electrode, and saturated calomel electrode as the standard half-cell. The resulting colors of the pigments of the two series are compared as to tint, strength, and mass tone. The method is discussed as a means of control of the color of lead chromate pigments.

The color of precipitated lead chromates has been shown by previous experimenters (*4, 9, 10, 12, 13*) to depend on the concentration of reacting substances, temperature, rate of mixing, and manner of washing. This variation in color has been described (*1, 5, 6, 8, 11*) as being due to the presence of basic salts with normal salts, and to variation in particle size.

The effect of hydrogen-ion concentration on the color of lead chromate has been investigated by Ernst, Pragoff, and Litkenhous (*3*). Their results show that, using lead acetate and potassium dichromate while varying the pH of the lead acetate by means of acetic, nitric, hydrochloric, and sulfuric acids, and potassium hydroxide, the resulting lead chromates changed from medium yellows at a pH of 5 to orange at a pH of 9. Their investigation covered only chromates prepared from lead acetate and potassium dichromate.

A further study of the effect of pH on the color of lead chromates prepared from lead nitrate and lead acetate, and sodium dichromate and potassium dichromate was undertaken in order to ascertain if pH can be used to control the colors, and to indicate pH where the colors change from yellow to orange.

Experimental Procedure

The lead acetate and lead nitrate were prepared by repeated recrystallization of the pure salts from strongly acid solutions. The sodium and potassium dichromates were prepared by recrystallization from solutions of the c. p. salts. The acids and bases used were of highest purity.

The solutions used in these experiments were 0.5 normal, prepared in distilled water.

The hydrogen-ion concentrations of the solutions were determined by a potentiometric method (*3*), using the quinhydrone of Biilmann (*2*) as the indicator electrode, and saturated calomel electrode as the standard half-cell.

The lead chromates were prepared by precipitation from solutions having varying hydrogen-ion concentrations. Acids or bases were added to the lead nitrate or acetate solutions until the desired pH was obtained. The resulting solution was 0.5 normal and had a volume of 300 cc. To this solution were added 300 cc. of 0.5 *N* sodium or potassium dichromate. Thorough agitation of the solution took place throughout the precipitation. The precipitates were formed in 25 ± 2 seconds. The temperature was 25 ± 0.5° C. The solutions were agitated for 10 minutes after precipitation. The resulting pigments were allowed to stand until the precipitate settled, washed five times by decantation, filtered on a suction filter, and dried at 60° C. for 24 hours or until dry.

The resulting pigments were rubbed in bleached linseed oil to determine the mass tone, tints, and strengths. Tints and strengths were observed after mulling, 50 mg. of color, 1 gram zinc oxide, and 12 drops of linseed oil, 2 × 50 strokes (*3*).

The results of these experiments are given in Tables I to VI. The value for the potentiometer reading with the corresponding pH is given. The pH of the dichromate solutions corresponding to the observed values of the e. m. f. are probably not true pH values. All values above a pH of 9 are doubtful (*7*).

Table I. Effect of Variation of pH of Lead Nitrate Solutions with Nitric Acid and Potassium Hydroxide

(Potassium dichromate[a] added to lead nitrate solution)

	Lead Nitrate			Lead Nitrate	
Sample	pH	E. m. f.	Sample	pH	E. m. f.
		Millivolts			*Millivolts*
1[b]	4.0	−215	7	7.0	− 40
2	2.0	−333	8	8.0	+ 20
3	3.0	−275	9	9.0	+ 80
4	4.0	−215	10	10.0	+140
5	5.0	−157	11	11.0	+200
6	6.0	− 98			

[a] Potassium dichromate, pH 2.5 (e. m. f., −305 millivolts), not varied.
[b] Sample 1 is for 0.5 *N* lead nitrate solution.

Series I (Samples 2 to 11). When the pH of the lead nitrate solution is varied and potassium dichromate is used, the resulting lead chromates are medium yellows from a pH of 2 to 8. At a pH of 9 a decided change occurs, the resulting colors being orange. Sample 11 (pH 11) is the reddest of the oranges, while 10 is a "brownish off-shade." The tints and strengths below 9 are those of a medium yellow, 9 is light orange, 10 is "dark and dirty," and 11 is a medium orange.

Table II. Effect of Variation of pH of Lead Nitrate Solutions with Nitric Acid and Sodium Hydroxide

(Sodium dichromate[a] added to lead nitrate solution)

	Lead Nitrate			Lead Nitrate	
Sample	pH	E. m. f.	Sample	pH	E. m. f.
		Millivolts			*Millivolts*
12	2.0	−333	17	7.0	− 40
13	3.0	−275	18	8.0	+ 20
14	4.0	−215	19	9.0	+ 80
15	5.0	−157	20	10.0	+140
16	6.0	− 98	21	11.0	+200

[a] Sodium dichromate, pH 2.5 (e. m. f., −305 millivolts), not varied.

Series II (Samples 12 to 21). In this series the pH of the lead nitrate solution was varied with nitric acid and sodium hydroxide, and sodium dichromate was used. The mass tones are medium yellow with a change to orange at a pH of 9 (sample 19). Sample 20 (pH 10) corresponding to sample 10 is likewise off-shade, while 11 is redder than 21. The mass tones differ very little from series I. The tints and strengths are similar, but the chromates using sodium dichromate give a weaker and lighter color than those prepared from the corresponding potassium dichromates.

TABLE III. EFFECT OF VARIATION OF pH OF LEAD ACETATE SOLUTION WITH ACETIC ACID AND POTASSIUM HYDROXIDE

(Potassium dichromate[a] added to lead acetate solution)

SAMPLE	LEAD ACETATE pH	LEAD ACETATE E. m. f. *Millivolts*	SAMPLE	LEAD ACETATE pH	LEAD ACETATE E. m. f. *Millivolts*
22	6.5	− 67	27	8.0	+ 20
23	4.4	−239	28	9.0	+ 80
24	5.0	−157	29	10.0	+140
25	6.0	− 98	30	11.0	+200
26	7.0	− 40			

[a] Potassium dichromate, pH 2.5 (e. m. f., −305 millivolts), not varied.

SERIES III (SAMPLES 23 TO 30). The pH of the lead acetate solutions was varied with acetic acid and potassium hydroxide. The resulting chromates (using potassium dichromate) below a pH of 9 are yellower and lighter than the corresponding nitrate yellows. Those above a pH of 9 are brownish. The mass tones of this series are similar to the nitrate yellows below a pH of 9. Samples 28, 29, and 30 are on the orange side. They are browner than the corresponding nitrates and are less desirable colors. Sample 29 is off-shade. The tints and strengths of the yellows are comparable, 28 is similar to 9, 29 is stronger than 10, but 11 is redder than 30.

TABLE IV. EFFECT OF VARIATION OF pH OF LEAD ACETATE SOLUTIONS WITH ACETIC ACID AND SODIUM HYDROXIDE

(Sodium dichromate[a] added to lead acetate solution)

SAMPLE	LEAD ACETATE pH	LEAD ACETATE E. m. f. *Millivolts*	SAMPLE	LEAD ACETATE pH	LEAD ACETATE E. m. f. *Millivolts*
31	4.4	−239	35	8.0	+ 20
32	5.0	−157	36	9.0	+ 80
33	6.0	− 98	37	10.0	+140
34	7.0	− 40	38	11.0	+200

[a] Sodium dichromate, pH 2.5 (e. m. f., −305 millivolts), not varied.

SERIES IV (SAMPLES 31 TO 38). The chromates of this series were prepared from lead acetate and sodium dichromate. The pH of the lead acetate solution was varied by means of acetic acid and sodium hydroxide. The colors are similar to series III. The mass tones show medium yellows a little more yellow than series I and II. Samples 37 and 38 are lighter than 29 and 30, and also than 10 and 11. The oranges are not as good as the nitrate oranges. The tints and strengths are similar to series III.

TABLE V. EFFECT OF VARIATION OF pH OF SODIUM DICHROMATE SOLUTION WITH NITRIC ACID AND SODIUM HYDROXIDE

(Sodium dichromate added to lead nitrate solution[a])

SAMPLE	SODIUM DICHROMATE pH	SODIUM DICHROMATE E. m. f. *Millivolts*	SAMPLE	SODIUM DICHROMATE pH	SODIUM DICHROMATE E. m. f. *Millivolts*
39	2.0	−333	44	7.0	− 40
40	3.0	−270	45	8.0	+ 20
41	4.0	−215	46	9.0	+ 80
42	5.0	−157	47	10.0	+140
43	6.0	− 98	48	11.0	+200

[a] Lead nitrate, pH 4.0 (e. m. f., −215 millivolts), not varied.

TABLE VI. EFFECT OF VARIATION OF pH IN LEAD NITRATE SOLUTION WITH NITRIC ACID AND SODIUM HYDROXIDE

(Lead nitrate added to sodium dichromate solution[a])

SAMPLE	LEAD NITRATE pH	LEAD NITRATE E. m. f. *Millivolts*	SAMPLE	LEAD NITRATE pH	LEAD NITRATE E. m. f. *Millivolts*
49	2.0	−333	54	7.0	− 40
50	3.0	−270	55	8.0	+ 20
51	4.0	−215	56	9.0	+ 80
52	5.0	−157	57	10.0	+140
53	6.0	− 98	58	11.0	+200

[a] Sodium dichromate, pH 2.5 (e. m. f., −305 millivolts), not varied.

SERIES V (SAMPLES 39 TO 48). In this series the pH of the sodium dichromate was varied with nitric acid and sodium hydroxide. The colors are similar to other nitrates. The mass tones below a pH of 9 are a little redder than series I, and correspond more to series III. The oranges are redder and correspond to series I. The tints are more like the acetate series below a pH of 9, but the oranges correspond to the nitrates in shade and tint.

SERIES VI (SAMPLES 49 TO 58). In this series the lead nitrate was added to the sodium dichromate. The pH of the lead nitrate was varied by means of nitric acid and sodium hydroxide. The series shows but little change in mass tone and strength for the entire series. Samples 56 to 58 are just a trifle darker than 49 to 55. There are no oranges in the series. Series VI is redder than series II. The tint and strength of 57 and 58 are very good.

CONCLUSION

Lead chromates prepared from lead acetate and lead nitrate with varying pH, using sodium dichromate and potassium dichromate, result in medium yellows to a pH of 9, where a decided change to orange occurs, except in series VI. There is but little difference in the mass tone, strength, and tint of the medium yellows. The precipitated wet pigments of the acetate series are lighter than the corresponding nitrate series. The mass tone and tints of the acetate yellows are redder than the nitrate yellows. Above a pH of 9 a decided change occurs to orange with the exception of series VI. The change is very sharp and definite. The oranges of the nitrate series are brighter and redder in mass tone and are more desirable pigments.

Adding the lead nitrate to the sodium dichromate gives a redder mass tone and tint than the reverse, but the series are all medium yellows with no oranges. Varying the pH of the dichromate results in a nitrate series which is similar in mass tone and strength to the acetate.

The chromates, both in the case of lead acetate and lead nitrate using potassium dichromate, are a little stronger and darker in tint and strength than those from sodium dichromate, but there is less difference below a pH of 9. The acetate yellows are softer and grind into the oil more easily than the nitrate yellows. The potassium and sodium radical seems to have little effect on the hardness of the pigment.

The pH of the lead nitrate or lead acetate solution can be used as a means of control of color in preparing lead chromate pigments.

Further work is now in progress in this laboratory on the relation of pH, chemical constitution, and dispersion as related to the color of lead chromate pigments.

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Relative Toxicity of Some Fluorine and Arsenical Insecticides

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THE RELATIVE toxicity of fluorine and arsenical insecticides was determined by feeding to white rats various accurately measured amounts of cryolite, barium fluosilicate, and lead arsenate mixed with their food for 16 weeks. The results, including behavior, appetite, fecundity, growth, tooth development, and organ pathology, agree in indicating the arsenical compound used to be several times as toxic as the fluorine ones.

THE commercial production of fruit and vegetables is impossible without the use of some chemical product for the control of insect damage. The most frequently used materials are the various arsenates, applied in watery sprays. The use of such materials, recognized as toxic in some degree to humans, carries with it the necessity for removal of most of the insecticide remaining on the product before it can be marketed. Robinson in 1929 (*21*) described the troubles of the grower in reducing arsenic residue on fruits to the legal tolerance without so injuring the fruit that it becomes an easy prey for organisms causing decay. More recently Fisher (*11*) has stated that dilute hydrochloric acid can be effectively used in washing arsenical residues from apples.

Marcovitch in 1926 (*15*) pointed out that the use of fluorine compounds would avoid much of this difficulty because of their lower toxicity to man. Sollmann in 1926 (*25*) recorded the minimum lethal dose of arsenic trioxide to be about 0.1 gram for a man, and of sodium fluoride to be about 0.5 gram per kilogram body weight for a rabbit; Marcovitch in 1929 (*16*) gave that of sodium fluosilicate as 0.12 gram per kilogram for a rabbit. Reducing these to the same units, the arsenic trioxide is found to be about 250 times as toxic as the fluoride, or 60 times as toxic as the fluosilicate.

However, the toxicity quoted is the acute toxicity, that is, the single dose causing death. It is almost inconceivable that any person could eat enough sprayed fruit at one time to be acutely poisoned by the insecticides. For properly evaluating the hazard from spray residues, information on chronic toxicity is desired, that is, on the dose that will injure when repeated daily for long periods of time.

There is still more objection to the figures quoted above in that they do not represent the compounds actually used as insecticides. Arsenates are known to be less toxic than the trioxide (*29*), and the fluorine compounds used as sprays are so much less soluble than sodium fluoride that they have been suspected of being less toxic than the latter.

The literature on the chronic effects of arsenicals and fluorides is not so conclusive as that on their acute effects. In 1921 Sollmann (*24*) reported 0.00005 to 0.0005 mg. per kilogram body weight of arsenic trioxide in the diet of albino rats to have definite retarding effect on growth, and 0.0015 to 0.005 mg. per kilogram to have a greater effect, both after feeding for 9 to 14 weeks. O'Kane, Hadley, and Osgood in 1917 (*20*) fed guinea pigs lead arsenate at the rate of 1.7 to 11.9 mg. per day for 30 days without effect, and killed others with 13.6 mg. per day in 22 days. These quantities multiplied by three to reduce to milligrams per kilogram, based on average weight of a guinea pig, will approximately reduce their units to those of Sollmann, and give some idea of either the difference in experimental method, or of the difference in toxicity between the two compounds.

Almost all of the work with fluorides has been done with sodium fluoride. The literature (*3, 5, 6, 7, 12, 19, 22, 26*) is in general agreement that, when the diet of the white rats is about 0.02 to 0.03 per cent sodium fluoride, symptoms will be noticed after weeks of feeding, or when the dosage rate is about 30 mg. per kilogram body weight. Lewy in 1928 (*14*) fed calcium fluoride and killed mice after 6 to 9 months, but no definite dose was reported. Sodium fluosilicate is credited with the same chronic toxicity as the fluoride (*6, 7*). The symptoms noted with doses too small to kill are abnormal teeth (*19*), loss of weight, stopping of the sexual cycle (*4*), and general poor condition.

It is agreed that high fluorides in the human diet will cause dull and mottled teeth, but the dosage to produce this effect has not yet been determined (*23*).

This work was undertaken to determine the relative chronic toxicity of fluorine and arsenical insecticides when fed by mouth. Albino rats were used for test animals, primarily because their diet is varied as is man's, and therefore they can be expected to react to most toxic materials in the same general way that man would react. In addition, rats take up little room and require relatively little care, and they are so inexpensive that more can be included in an experiment than would be the case with larger animals. Their life cycle is so short that animals just weaned at the start of an experiment will have become parents once or twice when the experiment is finished a few months later. This permits observation of the effect of a poison in all stages of life.

Care of Test Animals

When received, the rats were quite young, being from 40 to 80 grams in weight. Young animals were used so that their growth curves would furnish information on toxic effects. They were placed in groups of six in metal cages with clean sawdust bedding, and were identified by a code formed of ear clips and sex. As soon as received, each one was weighed and the weighing was repeated weekly as long as they were kept. After one or more weeks of observation animals were selected which were apparently healthy; they were regrouped, if necessary, to put three males and three females in each cage. A total of 246 rats was used in the study, divided among 41 cages.

All pups born during the 16-week period of the test feedings were kept in the same cage with the parents and others of the group. It was realized that this was not the best treatment to keep a maximum of pups alive, but facilities were not available to care for the total of about a thousand pups which were born during the course of the tests. Many pups inevitably died or were eaten by the adults. When a cage became overcrowded, due to the survival of many pups, the latter were removed and killed to give the adults room.

Diet of the Animals

The basic diet used consisted of a mixture of 2 parts by weight of ground whole wheat, 1 part whole milk powder, and

0.04 part sodium chloride. This diet was found perfectly satisfactory for normal rat nutrition, for the control animals all gained weight at least as rapidly as the accepted standard curves demand (*10*), and were always healthy and well nourished. The diet was mixed in batches of 25 to 50 kg., and was fed to the rats in McCollum feed pans (*18*) to reduce loss and make it possible to determine the actual weight eaten by a cage of rats. A cage of six rats, close to 100 grams in weight, maintained normal growth on about 75 grams of this diet per day.

Each cage had a siphon water bottle attached to the side so that the animals could always reach adequate water, but were unable to foul it. A cage of six rats drank as much as 200 cc. per day.

Analyses of the basic diet were made for arsenic, lead, and fluorine.

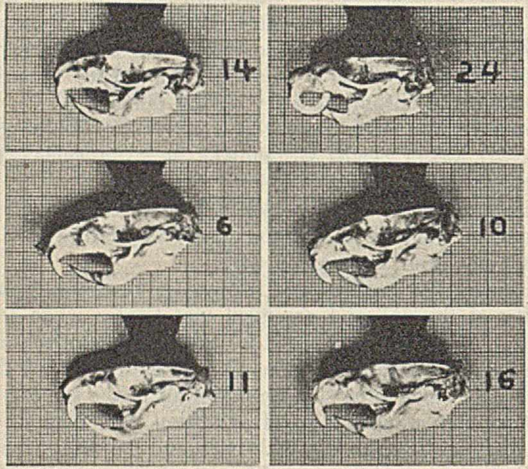

FIGURE 1. CONTROL AND TYPICAL SKULLS OF RATS RECEIVING FLUORINE COMPOUNDS

Numbers refer to cages from which rats came. Background ruled in millimeters.

Arsenic was tested for by the A. O. A. C. method (*2*), and none was found. The method, with the size sample used, should show anything above 0.01 mg. per 1000 grams of sample. Since the smallest dose fed was approximately 0.0006 mg. per 1000 grams of sample, the analytical method was not entirely adquate for the purpose. However, the method of analysis did show that the arsenic present in the basic diet was not sufficient to affect the size of the doses found toxic, since these harmful doses were all many times the smallest amount the test would detect.

Lead was tested for by chromate precipitation, followed by colorimetric determination with *sym*-diphenylcarbazide (*13*). No lead was found, which means that less than 0.01 mg. was present per 1000 grams of sample. The smallest dose fed included only 0.004 mg. per 1000 grams of basic diet, but the analytical result was sufficient to prove that no lead in the diet affected the size of doses found toxic.

Fluorine was estimated by the method of Treadwell and Kohl (*28*). Ten p. p. m. fluorine were found in the basic diet. It is felt that the method is not particularly reliable for such small amounts, and no confidence is felt in the absolute value of this fluorine content although it is probably somewhere near the truth. This amount of fluorine is approximately equal to a dosage of 1.4 mg. per kilogram of cryolite, and 1.5 mg. per kilogram of barium fluosilicate. Accordingly, this amount was added to each calculation of dosage of the two materials to correct for fluorine in the basic diet.

FEEDING THE INSECTICIDES

The materials used for feeding were cryolite, barium fluosilicate, and lead arsenate, in grades available for insecticide use. As materials suitable for spraying fruits were the ones of most interest, calcium arsenate was not included. The purity of the compounds was determined by the A. O. A. C. methods (*1*) and according to Treadwell (*27*), and the results are entered in Table I.

Seven control cages received the basic diet without the addition of any chemical, while thirty-four cages received various doses of the insecticides. The doses fed were planned to give comparative results between the four materials, and were based on the results quoted above. After the work had had been under way for some time, it was seen that the arsenic doses were too small to give definite effects, so larger doses had to be added. These larger doses, starting later, were fed for shorter times than the original doses. A further series of tests is contemplated covering longer feeding times. Table I gives the doses which were fed, calculated for the pure chemical compound and corrected for fluorine in the basic diet, and the number of weeks the feeding was continued.

Each week a calculation was made for each cage under treatment so that the proper amount of the toxic material might be added to that week's diet. This calculation took into account the dosage desired for the cage, the weight of the animals, the amount of food they had eaten the week before, and any deficit in dosage experienced during previous weeks.

The calculated amount of the toxic material was then weighed out (as a 0.1, 1, or 10 per cent mixture with ground wheat) and was mixed with enough of the basic diet to feed the cage for 7 days. The two were mixed thoroughly in a wide-mouth glass jar, and the food was kept in this jar until the end of the week.

Each day the food pans were filled from their respective jars. At the end of the week any food remaining in the food pans was returned to the jars, and the total uneaten food was weighed. From the actual amount of food eaten, the amount of toxic material in the food batch, and the average weight of the animals during the week, the true dosage during that week was calculated, and the average dosage to date from the start of the tests, assuming that each rat ate the same amount. The true weekly dosage seldom agreed perfectly with the desired dosage, necessitating adjustment during the following week to keep the average dosage fairly constant.

No calculations of the dosages in terms of parts per million of the diet were made, although sufficient data for such calculations are available if results in such terms prove necessary. All calculations and reports of dosages are in terms of milligrams of toxic material per kilogram body weight of the animals, administered daily. For approximate conversion of these results to parts per million of the diet, they may be multiplied by twelve. This constant is valid only for this report and is based on the average amount of food eaten and average animal weight.

KILLING THE ANIMALS

Rats surviving the feeding period were all killed for autopsy by cutting the spinal cord with a heavy scalpel. They were promptly autopsied, and, in general, kidney, liver, spleen, and sciatic nerve were taken for examination. In some cases lungs were also taken. Where it was possible to get organs of four animals from one cage, all free from pneumonia or other infection, only such organs were used. However, in some cases there were not four animals free from infection in a cage. Then diseased animals had to be studied.

These organs were mounted according to the usual histological technics, and microscopic preparations of all were studied for evidence of toxic degeneration in the light of an

Table I. Summary of Doses Fed and Results Obtained

				Symptoms of Toxic Action						Authors' Judgment of Toxic Action		
Material Fed	Cage	Time Fed	Dosage Calcd. to 100% Basis	Appearance	Appetite	Growth	Fecundity	Teeth	Organ degeneration	None	Possible	Definite
		Weeks	Mg./kg.									
Cryolite, 94.3% Na_3AlF_6	1	16	6.3	..	..	..	..	..	..	+	..	..
	6	16	11.6	..	..	..	..	..	..	+	..	..
	10	16	21.8	..	..	..	?	?	..	..	+	..
	15	16	42.5	..	?	..	?	+	?	..	..	+
	19	16	78.9	+	+	+	+	+	+	..	..	+
	24	16	158.	+	+	+	+	+	+	..	..	+
Barium fluosilicate, 99.5% $BaSiF_6$	2	16	4.5	..	..	..	..	..	..	+	..	..
	7	16	7.5	..	..	..	..	..	..	+	..	..
	11	16	13.1	..	..	..	..	..	..	+	..	..
	16	16	28.1	..	..	?	..	?	..	..	+	..
	20	16	50.6	..	?	+	+	+	+	..	..	+
	25	16	98.	+	+	+	+	+	+	..	..	+
Lead arsenate, 96.0% $PbHAsO_4$	8	16	0.00099	..	..	..	..	..	..	+	..	..
	12	16	0.00405	..	..	..	..	..	..	+	..	..
	17	16	0.0171	..	..	..	..	..	..	+	..	..
	21	16	0.064	..	..	..	..	..	..	+	..	..
	26	16	0.265	..	..	..	..	..	..	+	..	..
	28	11	1.03	..	..	..	..	..	?	..	+	..
	31	8	3.93	..	..	..	..	..	+	..	..	+
	32	8	16.7	..	..	..	..	..	+	..	..	+
	39	4	59.5	+	..	+	..	..	+	..	..	+
	40	4	116.	+	..	+	..	..	+	..	..	+

extensive experience with the pathology of experimental animals. Permanent preparations of all the organs are filed, but the degenerations seen were not sufficiently characteristic or unique to make photomicrographs of value.

Results of the Feeding

Space is not available for a discussion of the results obtained with each cage of animals. Table I lists the symptoms and direct evidence of toxic action which were found. A plus mark in this table means that animals in the cage in question were definitely injured by the dose fed as far as the particular symptom is concerned. A question mark means a doubtful or inconclusive effect.

Behavior and Appearance of Treated Animals. Aside from animals later found to have advanced pneumonia, only the larger doses of the insecticides appeared to have any effect on the behavior or general appearance of the rats. This effect was seen as roughness and unkempt appearance of the coat which is characteristic of sick rats; normal rats always having smooth clean coats. Upon handling the animals, they felt flabby, in marked contrast to the firm elastic feel of healthy rats. This effect on the animals did not proceed so far as to make them less active or less interested in changes in their surroundings than are normal rats.

Appetite. Because of the fact that pups were left in the cages with the adults until they were several weeks old, no accurate calculations of food eaten per animal are possible. The population of the cages changed so often that such a calculation would be very intricate, and it is impossible to tell how much of the food was eaten by adults and how much by weaned pups. However, from the records of food eaten by each cage, some idea of appetite was gained even when an absolute measure of it was impossible. The entries in Table I are based on this evidence.

Rate of Growth. All rats used were quite young, so all should have gained weight regularly according to definite curves (*10*) throughout the test period. The larger doses of all the materials produced some degree of retardation in growth. This was sufficiently marked in some cases to be plainly evident from casual examination of the animals.

It should be pointed out that a deviation of a few per cent from the weight of the control animals does not necessarily have any significance. The control animals themselves differed from each other by as much as 20 per cent at the same age, so that even in a moderately large group considerable variation in average weight would be expected.

With the arsenical doses there is some indication of a stimulation of weight gained by the dose, as might be expected from the pharmacological use of arsenic compounds.

Fecundity. Only five single cages had as high a ratio of embryos to females as the controls, so that probably almost every dose had some effect on fecundity. The smallest doses, however, were not the ones to come nearest the controls, so that few dose limits can be drawn for this effect. Taking all of one material together, cryolite came farthest from the controls. However, since the lowest arsenical dose was about one-seven-thousandth of the toxic dose and the lowest fluorine dose only one-eighth of the toxic dose, this comparison is not fair to the fluorine compounds.

Tooth Development. Figure 1 shows the effect of fluorine compounds on tooth development, pointed out in 1925 by McCollum (*19*). The teeth of the animals receiving arsenical compounds were all completely normal. The effect noticed is an apparent stimulation of tooth growth, producing in the extreme such monstrous teeth as are illustrated for cage 24. In reality the cause is poor bone development in the lower jaw, which prevents the upper and lower teeth from wearing each other off as they do in normal animals. Since the teeth of rats grow continuously, the upper teeth make more and more of a circle as the amount of fluoride is increased until, as in cage 24, they touch the upper jaw. There is nothing to prevent the teeth penetrating the upper jaw in time, or with increased dosage of fluorine compounds.

In the figure, cage 14 is the control cage and the teeth are normal. Cages 6 and 11 received doses of cryolite and fluosilicate, which had no effect on the teeth at all. Cages 10 and 16 received the next higher doses, and the teeth are just beginning to be long. In addition, these teeth had the chalky patches recognized as a probable human symptom of fluorine excess (*8*).

Pathology of Organs. No tissue studies were made on the organs of animals showing pneumonia upon autopsy, unless it was not possible to obtain tissues from at least two other animals out of each cage of six. As a rule, tissues of at least four animals out of each cage of six were studied microscopically and are included in this paper.

Microscopic study of the pathology of the organs is the most important phase of a problem such as this, but details of pathology found cannot be given here because they cannot be expressed numerically, and space is not available for extended discussion. The types of liver and kidney degenerations found were no different from those caused by most toxic materials. In the higher doses the fluorine compounds caused marked kidney degenerations but had no effect in the lower doses. Some of the higher arsenic doses produced slight nerve degenerations, but none of the fluorine doses did this.

DEATHS AND DISEASE. Deaths and pneumonia were encountered among animals receiving all the test materials, but the number of animals affected in any one cage was too small for any statement about definite doses. In 35 per cent of the animals fed the arsenical compounds, pneumonia, liver parasites, or inflamed eyes were found; and 38 per cent of the animals fed fluorine compounds were similarly affected. There was, therefore, no specific effect from either of the materials on the infections. No animal died during the feeding from the effects of doses alone, for all those dying were found to be infected in some way.

SUMMARY

In the tabulation below, the doses are in terms of milligrams of the compound on a 100 per cent basis per kilogram body weight of the animal, fed daily for 16 weeks; or, if for a different period, the weeks follow the dose in parantheses.

	CRYOLITE	BARIUM FLUOSILICATE	LEAD ARSENATE
No evidence of harm	11.6	13.1	0.265
Questionable effect	21.8	28.1	1.03 (*11*)
Definitely toxic	42.5	50.6	3.93 (*8*)

Pound for pound, the chronic toxicity of the materials tested is shown by this work to be in approximately the following relation, based on doses given above as definitely toxic:

	TOXICITY %
Lead arsenate	100
Cryolite	10
Barium fluosilicate	8

Or the daily doses necessary to give the same definite chronic effect would be in approximately the following relation:

Barium fluosilicate	13
Cryolite	11
Lead arsenate	1

Calculating the equivalent fluorine and arsenic trioxide dosages for the compounds actually fed, it is seen that a dosage of 23.1 mg. fluorine per kilogram as cryolite, or 20.6 as barium fluosilicate, is the lowest dose found definitely toxic, while an equal degree of toxicity was obtained by 1.12 mg. arsenic trioxide per kilogram as lead arsenate. As a margin of safety in this reasoning, it must be borne in mind that the effects with arsenic were obtained in 8 weeks, while those of the fluorine were had in 16 weeks. From these figures, the lead arsenate was about 18 times as toxic as the barium fluosilicate when calculated in terms of arsenic trioxide and fluorine, respectively.

When expressed in terms of fluorine, cryolite and barium fluosilicate have substantially the same toxic doses. The results with these compounds are in accord with the literature, when expressed in terms of fluorine doses, although the literature deals almost entirely with the soluble compound—sodium fluoride. In particular, McClure and Mitchell (*17*) in 1931 reported 0.03 to 0.04 per cent fluorine in the diet of rats to be the threshold for abnormalities of bone structure. Reduced to the dosage units of this report, this is about 25 mg. per kilogram, or close to the figure given as definitely toxic in the paragraph above, and producing definite abnormality in tooth growth, which depends on the bony structure of the jaw. It is thus apparent that the chronic toxicity of cryolite and barium fluosilicate is proportional to their fluorine content. The chronic toxicity of these compounds is substantially the same as that of sodium fluoride for the same fluorine content.

CONCLUSION

Taking the materials tested to be representative of arsenical and fluorine insecticides in general, the results obtained over the period of these tests indicate that several times as much fluorine compound is needed as arsenical compound to give the same chronic toxic effect from repeated doses.

It would seem that the use of fluorine insecticides would leave a much wider margin of safety than do arsenical materials between the weight of spray residue on fruit and the amount toxic to the consumer.

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FABRICS NOT WEAKENED BY CLEANING SOLVENTS. A series of tests conducted by the Bureau of Standards at the request of the cleaners and dyers industry proved that exposure to light and heat rather than the chemical action of solvents weakens fabrics.

The series of tests indicated that all fabrics were weakened by repeated cleaning, but that the loss of strength was in ratio to the time the materials were exposed to light and heat rather than any influence the solvents might exert upon the fabrics, according to Warren E. Emley, chief, Organic and Fibrous Division of the bureau.

Details of the numerous tests will be published shortly by the Bureau of Standards.

At the suggestion of the National Association of Dyers and Cleaners, the Bureau of Standards began a series of tests in April, 1931, and continued them through December, 1931, in an effort to determine the effect of solvents on different materials under different conditions.

According to Mr. Emley, tests were made on materials soiled with carbon black, paint, tea, sirup, gravy, and lip stick. It was found that certain solvents were more efficient on certain types of soil in relation to the kind of material being cleaned. It was also found that the amount of moisture in the material being cleaned had a decided influence on the efficiency of some solvents.

Volatilization of Potash from Potassium Aluminum Silicates

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AS A SOURCE of agricultural potash the large deposits of potassium aluminum silicates are valuable in so far as their potash can be extracted economically. It is shown that the potash can be successfully extracted from the potassium aluminum silicates by means of a combination of $CaCO_3$ and $CaCl_2$ at temperatures from 1200–1500° C. A mixture consisting of silicate, $CaCO_3$, and $CaCl_2$ gives a volatilization of 87 to 99 per cent. By employing these potassium aluminum silicates together with $CaCO_3$ in simple ratios, 1:2 to 1:3 by weight, and adding to these one K_2O equivalent of $CaCl_2$, a cement mixture is obtained which, when treated in an ordinary rotary kiln, results in a Portland cement. The potash comes off as KCl vapor and can be collected by means of a precipitator. The yield of K_2O varies from 11.51 to 22.23 pounds per barrel of cement from greensand and Wyoming leucite, respectively.

The large deposits of potassium aluminum silicates occurring in various parts of the United States represent potential sources of agricultural potash whose importance is to be measured in terms of the feasibility of extraction methods devised for their processing. These silicates (*16*) are represented by the greensand of New Jersey, Delaware, Maryland, and Texas; the leucite of Wyoming (wyomingite); the shale of Georgia; and feldspar occurring in the industrial east and agricultural south. Many attempts have been made in the past to extract the potash from these minerals. Methods heretofore attempted can be divided into two classes: acid or base-exchange extraction in an aqueous medium; and pyrolytic methods. The latter can again be divided into two groups: volatilization of the potash as a halogen salt by smelting the potash-bearing rock together with $CaCl_2$ or NaCl in a blast furnace, using coke as a source of heat (*2, 3, 4, 9, 13*); and its volatilization in the same form in a rotary cement kiln by using the potash-bearing rock together with a halogen salt as a part of the charge for cement manufacture (*5, 10, 11, 12, 14, 15*). The present work was undertaken as a study of the conditions most suitable for pyrolytic extraction of potash, whether in a blast furnace or a cement kiln.

In a previous paper (*7*) a series of experiments was described showing the effect of $CaCO_3$, $CaCl_2$, NaCl, CaF_2, time, and temperature on the volatilization of potash from wyomingite. In the present paper are presented further studies of potash volatilization from wyomingite and particularly from greensand, shale, and feldspar, with or without various promoters.

In each case, except where variations are noted, the following procedure was employed: The mineral was ground to pass a 100-mesh screen and was dried for 15 hours at 140° C. The promoter where used was thoroughly mixed with the pulverized mineral treated and heated at 1510° C. for 40 minutes in a platinum crucible. The furnace employed is described in the preceding paper (*7*). In each case losses in weight were observed and residue analyzed for loss in K_2O.

Temperature Effect on Volatilization of K_2O from Wyomingite

The wyomingite employed was of the following composition:

	%		%
SiO_2	51.34	CaO	5.07
K_2O	12.76	P_2O_5	1.97
Al_2O_3	11.68	TiO_2	2.12
Fe_2O_3	4.90	Na_2O	1.42
MgO	6.92		

It was found in the previous paper that, by heating wyomingite at 1510° C. without promoters, the average amount of K_2O volatilized in six runs was 28.18 per cent. In these experiments temperature was varied from 1010° to 1410° C. Table I shows the results of all these runs. The material was found molten at 1210° C.

Effect of $CaSO_4$ on Volatilization of Potash from Wyomingite

In this series wyomingite was heated with various amounts of $CaSO_4$, from 0.25 to 2.00 equivalents of the K_2O content of the wyomingite. The results are shown in Table II. In all these runs the material was found molten at 1510° C.

As compared with the effect of $CaCl_2$, NaCl, CaF_2, and $CaCO_3$ on volatilization of K_2O from wyomingite studied in the previous paper, $CaSO_4$ not only does not promote volatilization but, on the contrary, retards it. Whereas without promoters 28.18 per cent K_2O leaves the wyomingite in 40 minutes at 1510° C., with $CaSO_4$, all the other conditions being the same, volatilization is lowered considerably. With $CaCl_2$ as promoter, half an equivalent of $CaCl_2$ gives 30.33 per cent, and 2 equivalents give 81.50 per cent K_2O volatilization. With other promoters, the amounts of K_2O volatilized for 0.5 and 2 equivalents are 38.32 and 65.20 per cent for NaCl, and 32.60 and 57.37 per cent for CaF_2. In the case of $CaCO_3$ the amounts volatilized are 28.61 per cent for ratio,

$$\text{Wyomingite}:CaCO_3 = 1:0.5$$

and 30.72 per cent for a ratio 1:1. In terms of K_2O equivalents of $CaCO_3$, amounts volatilized are about 28.2 per

Table I. Volatilization of Potash from Wyomingite

(Heating at 1510° C.)

Expt.	Temp.	K_2O Volatilized	Expt.	Temp.	K_2O Volatilized
	° *C.*	%		° *C.*	%
61	1010	0	16	1510	16.4
61a	1010	0	17	1510	19.2
62	1307	0	18	1510	16.6
63	1310	0	19	1510	18.3
63a	1310	0	24	1510	18.6
64	1410	7.0	25	1510	18.8

Table II. Effect of $CaSO_4$ on Volatilization of Potash from Wyomingite

(At 1510° C.)

Expt.	$CaSO_4$–K_2O Equivalent	K_2O Volatilized
		%
Av. from 6 runs	0	28.18
65	0.25	13.73
66	0.50	13.48
67	1.00	14.98
68	1.50	16.85
69	2.00	16.38

cent for promoter additions up to 3.7 equivalents, and 42.79 per cent for 14.7 equivalents.

In studying volatilization of potash from cement mixtures in the rotary kiln, Anderson and Nestell (*1*) found that the presence of SO_2 in the gases in contact with the materials retards the volatilization of the potassium salts. It is quite likely that the reason for this lies in the fact that K_2SO_4, which would form in the presence of sulfur dioxide, has a low vapor pressure at the temperatures in question so that little of it will come off as a vapor.

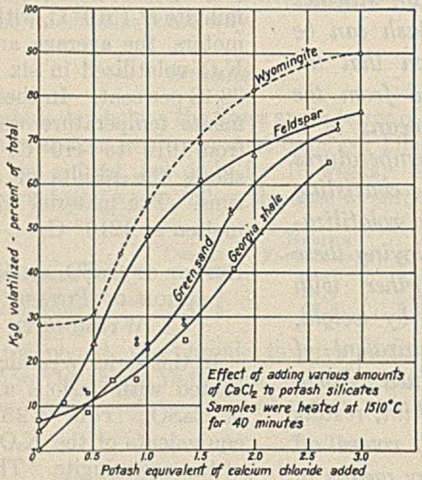

FIGURE 1

In studying the actual losses in weight obtained in these experiments from weighing the samples before and after heating, it is found that, after allowing for losses due to volatilization of K_2O, on the average about 66 per cent of the original weight of $CaSO_4$ is lost. Assuming that all of the $CaSO_4$ decomposes into CaO and SO_3, the loss would be 70 per cent, which indicates that most of the $CaSO_4$ decomposed.

VOLATILIZATION OF POTASH FROM GREENSAND

The following analysis shows the composition of the greensand used in these experiments:

	%		%
SiO_2	47.35	Fe_2O_3	30.02
K_2O	7.23	MgO	1.43
Al_2O_3	8.36	CaO	1.35

When heated without promoters no volatilization of K_2O from greensand took place, as shown in Table III.

TABLE III. VOLATILIZATION OF POTASH FROM GREENSAND (At 1510° C.)

EXPT.	GREENSAND	$CaCl_2$–K_2O EQUIVALENT	$CaCO_3$	K_2O VOLATILIZED
	Gram		*Gram*	%
70	1.0	0	0	0
71	1.0	0	0	0
72	1.0	0	0	0
73	1.0	0.45	0	12.86
74	0.5	1.00	0	21.30
75	1.0	0.90	0	23.93
76	0.5	1.00	0	23.37
77	1.0	1.34	0	28.07
78	1.0	1.78	0	53.25
79	1.0	2.79	0	72.41
81	0.5	0	0.5	18.26
82	0.5	0.5	0.5	65.14
80	0.5	1.0	0.5	94.88
133	0.5	1.0	0.5	85.76
83	0.5	1.5	0.5	99.58
84	0.5	2.0	0.5	99.72

As promoters, $CaCl_2$ alone and $CaCl_2$ mixed with $CaCO_3$ were employed in varying amounts. The volatilization obtained is shown in Table III. In Figure 1 the effect of $CaCl_2$ alone on volatilization of K_2O from greensand is shown. In Figure 2 the effect of adding $CaCl_2$ and $CaCO_3$ is shown. In both figures the dotted curves represent volatilization of K_2O from wyomingite and are introduced here for comparison. It is seen that a combination of 1:1 greensand and $CaCO_3$ by weight and one potash equivalent of $CaCl_2$ gives a K_2O volatilization of over 90 per cent. In all the experiments listed in Table III, after accounting for losses in weight due to volatilization of K_2O, to loss of CO_2 from $CaCO_3$, and to volatilization of unreacted $CaCl_2$, the actual loss in weight after heating shows an average excess loss of 7 per cent, which can be ascribed principally to water of hydration and organic matter. In all these runs the material was found molten.

In order to determine the influence of temperature on volatilization of K_2O from greensand, 0.5-gram samples of the mineral, mixed with 0.5 gram $CaCO_3$ and one K_2O equivalent of $CaCl_2$, were kept at various temperatures for periods of 40 minutes. Table IV and Figure 3 show the results.

TABLE IV. VARIATION OF VOLATILIZATION OF POTASH FROM GREENSAND WITH TEMPERATURE

EXPT.	TEMP.	K_2O VOLATILIZED
	° *C.*	%
103	910	12.30
104	1010	39.00
105	1110	80.49
106	1210	87.41
107	1310	93.09
108	1410	92.39
80	1510	94.88
133	1510	85.76

The dotted curve in Figure 3 represents the effect of temperature on volatilization of K_2O from wyomingite and was added here for comparative purposes. The greensand curve shows a sudden rise at about 1100° C. as does the wyomingite curve.

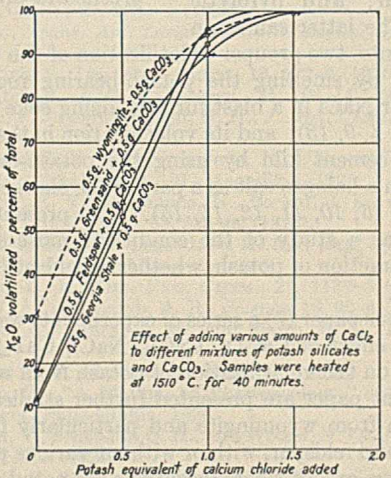

FIGURE 2

Losses of weight not accounted for are, in runs above 1100° C., about 7–9 per cent of the original weight of greensand, as in the other runs of the greensand series. In these experiments on greensand the samples were found well sintered at 1110° and completely molten at 1210° C.

VOLATILIZATION OF POTASH FROM GEORGIA SHALE

The Georgia shale employed, on analysis, showed the following composition:

	%		%
SiO_2	54.13	Fe_2O_3	12.63
K_2O	8.02	MgO	3.36
Al_2O_3	19.00	CaO	1.07

When heated without promoters at 1510° C. for 40 minutes, the mineral lost a small amount of its potash, as shown in Table V. On weighing the samples before and after heating it was found that 3.6 per cent loss in weight could not be accounted for after allowance was made for volatilization of K_2O, and is probably due to water of constitution not liberated at 140° C., and to organic matter.

TABLE V. VOLATILIZATION OF POTASH FROM GEORGIA SHALE

(At 1510° C.)

EXPT.	GEORGIA SHALE	$CaCl_2$–K_2O EQUIVALENT	$CaCO_3$	K_2O VOLATILIZED
	Gram		*Gram*	%
109	0.9	0	0	3.86
110	0.9	0	0	9.58
111	0.9	0	0	7.46
85	0.9	0.23	0	10.74
86	0.9	0.45	0	8.46
87	0.9	0.68	0	15.67
88	0.9	0.90	0	15.97
89	0.9	1.36	0	24.75
90	0.9	1.81	0	40.79
91	0.5	2.70	0	64.96
92	0.5	0	0.5	10.85
93	0.5	0.5	0.5	53.24
102	0.5	1.0	0.5	92.66
95	0.5	1.5	0.5	100.00
96	0.5	2.0	0.5	100.00

The effect of $CaCl_2$ alone and of $CaCl_2$ mixed with $CaCO_3$ is shown in Table V and Figures 1 and 2. As in the case of the other potassium aluminum silicates, the addition of $CaCO_3$ to a mixture of Georgia shale and $CaCl_2$ promotes volatilization considerably. In all the experiments listed in Table V (except 109, 110, and 111 where no promoters were employed) when actual losses in weight after heating are accounted for by losses due (1) to volatilization of KCl, (2) to volatilization of $CaCl_2$ above that which reacted with K_2O, and (3) to loss of CO_2 from $CaCO_3$, there is left, on the average, 1.7 per cent on the basis of original weight of Georgia shale which cannot be accounted for except as due to water and organic matter in the rock. In all of these runs the material was found molten.

The effect of temperature on volatilization of potash from Georgia shale is shown in Table VI and in Figure 3. In these experiments 0.5 gram Georgia shale, 0.5 gram $CaCO_3$, and one K_2O equivalent of $CaCl_2$ were intimately mixed and heated for 40 minutes at various temperatures. In this series of experiments, for runs above 1100, losses in weight not accounted for are, on the average, 3.2 per cent of the weight of Georgia shale used. The samples were found molten in cases when the temperature employed was above 1200° C.

TABLE VI. VARIATION OF VOLATILIZATION OF POTASH FROM GEORGIA SHALE WITH TEMPERATURE

EXPT.	TEMP.	K_2O VOLATILIZED
		%
97	910	38.18
98	1010	67.41
99	1110	83.83
100	1210	90.09
101	1310	94.65
94	1410	92.66
102	1510	92.66

VOLATILIZATION OF POTASH FROM FELDSPAR

The feldspar used in these experiments was of the following composition:

	%		%
SiO_2	63.87	Fe_2O_3	1.54
K_2O	12.18	MgO	0.61
Al_2O_3	14.27	CaO	1.46

The effect of heating feldspar alone without promoters is shown in Table VII. Here again, as in the case of Georgia shale, after allowing for the K_2O volatilized, 3.2 per cent of loss of weight from heating could not be accounted for, and might be due to H_2O and organic matter in the mineral.

The addition of $CaCl_2$ to feldspar has a more pronounced effect on volatilization of K_2O than in the case of Georgia shale or greensand, but not as great as in the case of wyomingite. In studying this effect, 0.5-gram samples of feldspar were mixed with various potash equivalents of $CaCl_2$. Table VII gives the results of these experiments. The results are shown graphically in Figure 1.

TABLE VII. VOLATILIZATION OF POTASH FROM FELDSPAR

(At 1510° C.)

EXPT.	FELDSPAR	$CaCl_2$–K_2O EQUIVALENT	$CaCO_3$	K_2O VOLATILIZED
	Gram		*Gram*	%
112	0.5	0	0	3.04
113	0.5	0	0	4.59
114	0.5	0	0	5.42
121	0.5	0.50	0	23.89
122	0.5	1.00	0	48.19
123	0.5	1.50	0	61.00
124	0.5	2.00	0	66.66
125	0.5	3.00	0	76.43
132	0.5	0	0.5	11.33
126	0.5	0.5	0.5	56.49
127	0.5	0.5	0.5	56.32
128	0.5	1.0	0.5	99.15
129	0.5	1.0	0.5	93.10
130	0.5	1.5	0.5	100.00
131	0.5	2.0	0.5	100.00

TABLE VIII. VARIATION OF VOLATILIZATION OF POTASH FROM FELDSPAR WITH TEMPERATURE

EXPT.	TEMP.	K_2O VOLATILIZED
	° *C.*	%
115	910	27.91
116	1010	64.04
117	1110	80.46
118	1210	90.80
119	1310	96.06
120	1410	94.00
128	1510	99.15
129	1510	93.10

The combined effect of $CaCl_2$ and $CaCO_3$ is shown in Table VII and Figure 2. In this series of experiments 0.5 gram feldspar was intimately mixed with 0.5 gram of $CaCO_3$ and various K_2O equivalents of $CaCl_2$, and the mixtures heated at 1510° C. for 40 minutes.

The actual loss in weight for the experiments listed in Table VII, except 97, 98, 99, where no promoters were employed, are greater than can be accounted for by losses of KCl, $CaCl_2$, and CO_2 by 1.6 per cent of the original weight of feldspar. This unaccounted loss might be due to water and organic matter. The feldspar curve in Figure 2 runs quite close to that of Georgia shale. In all the runs given in Table VII, the samples were found molten.

Temperature effect on volatilization of K_2O from feldspar is about the same as in the case of Georgia shale. This effect is shown in Table VIII and graphically in Figure 3. For runs above 1100° C. the average loss in weight not accounted for is 2.8 per cent of the weight of feldspar.

As to the state of fusion of the mixtures in these runs, they were found completely molten when the temperature was above 1200° C.

VOLATILIZATION OF POTASH FROM HIGH-LIME MIXTURES

In an earlier publication by the writer (7) an investigation was made of the effect of $CaCl_2$ and $CaCO_3$ on volatilization of potash from wyomingite. In the tests described there, various potash equivalent amounts of $CaCl_2$ were added to mixtures of wyomingite and $CaCO_3$ in the ratios—1:0.5, 1:1, and 1:1.5. This series of experiments was now extended to include the addition of $CaCl_2$ to a mixture of wyomingite and $CaCO_3$ in the ratio of 1:2. In these experiments 0.5 gram wyomingite was mixed with 1 gram $CaCO_3$ and various K_2O equivalents of $CaCl_2$, from 0.3 to 1. The mixtures were heated at 1510° C. for 40 minutes. The results are shown in Table IX and graphically in Figure 4. It is seen that under these conditions almost 100 per cent volatilization of K_2O can be obtained.

TABLE IX. VOLATILIZATION OF POTASH FROM HIGH-LIME MIXTURES

(At 1510° C.)

EXPT.	$CaCl_2$–K_2O EQUIVALENT	K_2O VOLATILIZED %
134	0.30	74.13
135	0.50	84.16
136	0.60	90.75
137	0.70	92.63
138	0.75	93.97
139	0.80	95.06
140	0.85	95.22
141	0.90	94.04
142	0.95	96.08
143	1.00	97.26

DECOMPOSITION AND VOLATILIZATION OF CALCIUM CHLORIDE AT HIGH TEMPERATURES

The assumption was made in the previous paper (7) that in the potash volatilization experiments any $CaCl_2$ in excess of that which actually reacts with K_2O leaves the crucible as a vapor. In order to verify this assumption, $CaCl_2$ was heated at various temperatures, under similar conditions to those in the potash experiments. The results are shown in Table X. It appears from this table that at lower temperatures only a small amount of $CaCl_2$ volatilizes. Most of it either remains in the crucible undecomposed or decomposes by reacting with water from the air. At 1510° C. most of the $CaCl_2$ leaves the crucible as a vapor with the exception of a small amount which decomposes.

TABLE X. DECOMPOSITION AND VOLATILIZATION OF CALCIUM CHLORIDE AT HIGH TEMPERATURES

TEMP.	$CaCl_2$ USED	LOSS IN WT. DUE TO HEATING	$CaCl_2$ Left in crucible	$CaCl_2$ Vaporized	$CaCl_2$ Decomposed
° C.	Mg.	Mg.	%	%	%
1110	100	40.0	35	16	49
1110	200	36.7	70	6	24
1310	100	60.7	11	32	57
1310	200	103.5	24	27	49
1510	100	89.7	0	80	20
1510	200	185.4	0	86	14

CONCLUSION

It can be seen from the results of this investigation, as well as from the results given in the previous paper (7), that potassium aluminum silicates will readily give up their potash, provided there is a sufficient amount of lime and chloride present in the mixture, and the temperature is raised above 1200° C. Mixtures made up of the silicate and $CaCO_3$, in the ratio of 1:1 by weight, and $CaCl_2$ molecularly equivalent to the K_2O content of the silicate, will give a potash volatilization of 87–99 per cent.

For many years it has been known that a considerable portion of the potash naturally present in the raw materials employed in cement manufacture is volatilized in the cement kiln and is carried out as a finely divided fume. Ross and coworkers (*14*), on the basis of their analyses of the raw mix and clinker from 104 cement plants of the United States and 9 of Canada, have shown that the raw materials contain an average of 0.7 per cent K_2O, of which 47 per cent is volatilized, approximately 2 pounds K_2O per barrel of cement, or 85,000 tons K_2O for the industry as a whole. This represents the amount of potash annually available when no regard is had for the potash content of the raw mix or for means of increasing the volatilization. The results presented in this paper and its predecessor show that this volatilization may easily be doubled by the addition of a promoter, and that, by the use of the potash silicates as raw material where economically available, the potash output can be greatly increased.

It was shown in the earlier paper that a mixture of wyomingite and $CaCO_3$ in the ratio of 1 to 2 by weight gave a volatilization of 42.79 per cent, which is in good agreement with the average, 47 per cent, reported by Ross and coworkers. The addition of one K_2O equivalent even to 1:1 silicate–$CaCO_3$ mixture gave a volatilization between 87–99 per cent.

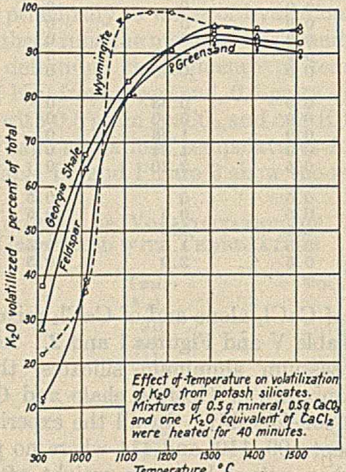

FIGURE 3

The engineering aspects of the problem were placed under widespread and intensive investigation during the war years of potash scarcity, with varying degrees of success. Researches conducted during the intervening years have advanced this technic to a degree where it may now be said that the problem of separating the potash fume from the particles of cement dust proper appears to be solved both technically and economically. Economic justification is found apparently in the value of the cement dust recovered and returned to the kilns, the potash incidentally secured becoming a by-product of very low cost.

The application of the potassium aluminum silicates to cement manufacture, in terms of raw mix and potash recoverable, is illustrated in Table XI. These data are based on the analyses of the respective silicates reported in this paper as well as on the volatilizations experimentally obtained. It was shown experimentally, in the case of wyomingite, that by using a rock–$CaCO_3$ ratio of 1:2, and one K_2O equivalent of $CaCl_2$, almost all of the potash was volatilized. The potash naturally comes off as a chloride. On treating the KCl with H_3PO_4, a double fertilizer of potash and phosphorus will be obtained, and HCl will come off. The HCl can be absorbed in

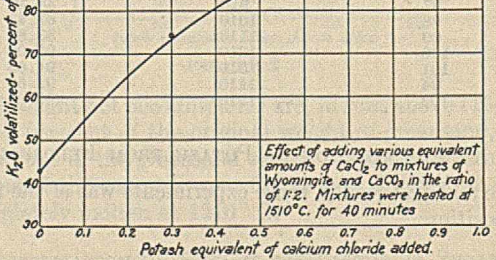

FIGURE 4

$CaCO_3$ to regenerate $CaCl_2$ and the chlorine thus utilized cyclically.

Table XI. Cement Composition and Potash Yield

	Cement				
	Av. Portland (*6*)	From wyomingite	From greensand	From Georgia shale	From feldspar
Raw mix:					
Rock : $CaCO_3$	...	1:2	1:2.5	1:2.5	1:3
$CaCl_2$, % of raw mix	...	4.78	2.39	2.64	3.46
K_2O, % of raw mix	...	4.05	2.03	2.23	2.94
Finished product:					
SiO_2, %	21.8	25.7	20.0	22.4	24.9
Al_2O_3, %	6.5	5.9	3.2	8.1	5.6
Fe_2O_3, %	2.9	2.5	12.6	5.6	0.7
MgO, %	2.4	3.5	0.7	1.6	0.2
CaO, %	63.3	62.4	63.5	62.3	68.6
$CaO:SiO_2$	2.90	2.43	3.17	2.78	2.76
K_2O yield,[a] lb. per barrel	...	22.23	11.51	13.39	16.71

[a] On the basis of 95% volatilization.

It is clear from Table XI that, when the various potash-bearing minerals are substituted for clay in the manufacture of Portland cement, the resulting product has about the same composition as ordinary cement. The only exception is cement from greensand which would have a high iron content—namely, 12.6 per cent Fe_2O_3 as compared with 2.9 per cent in Portland cement. However, high-iron cement has certain applications, such as for marine construction. According to Meade (*8*), the Krupp Steel Company of Hemmoor, Germany, is manufacturing an "Erz cement" intended for marine purposes. This cement has the following composition:

	%		%
SiO_2	20.5	Magnesia	1.5
Al_2O_3	1.5	Lime	63.5
Iron oxide	11.0	SO_3	1.0

This cement when mixed with plaster and exposed to the action of concentrated sea water of five times normal strength, under pressure of 15 atmospheres, showed no trace of expansion and contraction. Ordinary Portland cement would be destroyed under such conditions in a few days.

Acknowledgment

The writer wishes to express his indebtedness to J. W. Turrentine whose numerous suggestions and kind interest have been of great help in the course of this investigation, and to Miss E. Z. Kibbe for analysis of the potash aluminum silicates used in this work.

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Butyl-Acetone Fermentation of Corn Meal

Interrelations of Substrate and Products

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The fermentation of corn mash by *Clostridium acetobutylicum* (Weizmann) offers a striking example of the great rapidity of certain bacteriological processes. Within 60 to 70 hours after inoculation, provided conditions are favorable, the starch of the corn is changed into gases, acids, solvents, and small amounts of other compounds. The major products of this fermentation are: gases—carbon dioxide and hydrogen; solvents—acetone, butyl alcohol, and ethyl alcohol; and residual acids—mainly acetic and butyric. At the same time that these fermentation products are being formed, there is a marked hydrolysis of the proteins of the corn, with the formation of soluble proteins, proteoses, peptones, and amino acids. Papers by various investigators (*3, 5, 13, 14, 18, 19, 22, 24*) have dealt with one or more of these products, but their concurrent formation during the course of the fermentation has not been followed and correlated with changes in the carbohydrate and protein content of the medium. Likewise but little work has been published on the bacteriological changes which take place during the fermentation.

In this investigation it was planned to take frequent samples from the same body of fermenting mash throughout the fermentation, and to make all chemical and bacteriological analyses on the same sample. With certain exceptions this has been accomplished. From the data thus obtained it was hoped that a more unified and accurate picture of the whole process could be constructed than has hitherto been possible.

Experimental Procedure

Inoculum and Samples. A 50-liter round-bottom Pyrex flask, containing 40 liters of sterilized 6 per cent corn mash, was seeded with 1000 cc. of a 24-hour culture of *Cl. acetobutylicum,* strain 105. Immediately after inoculation, the contents of the flask were mixed thoroughly and 3000 cc. were withdrawn for bacteriological and chemical analysis. At intervals of 3 hours during the early stages, and later at longer intervals, 1500-cc. samples were drawn and aliquots taken for the several determinations. Apparently the agitation of the large culture prior to drawing each sample had no injurious effect on the fermentation, for the yield of solvents was about the same as that given by undisturbed cultures.

Bacteriological Methods. The total number of bacteria was determined in direct microscopic mounts by the Breed and Brew method (*2*), and the number of viable cells by dilution counts. For each direct count 3 smears were made. These were stained respectively with Ziehl's carbol fuchsin diluted 1 to 5, Gram's stain, and Dorner's modified nigrosine stain. From the first two smears the total number of bacteria and of clostridia were obtained, and from the third mount the number of spores was calculated. The dilution counts were carried out in deep tubes of freshly steamed corn mash. Because of the difficulty in securing growth of *Cl. acetobutylicum* from a small inoculum, an aerobic form of the *B. mesentericus* group was added to each tube to favor growth of the anaerobe by the principle of associated growth. The growth of the two organisms in corn mash is so different that there is no danger of mistaking one for the other.

Activity of the culture was measured by the rate of methylene blue reduction. One cubic centimeter of methylene blue solution, containing 2.5 mg. of the dye, was added to 20 cc. of glucose-peptone medium in tall test tubes. The figures on the chart represent the time in minutes required to reduce the methylene blue when 1 cc. of culture was added to each tube.

The life cycle of the bacteria (vegetative cells, clostridia, and spores) was followed by means of wet unstained mounts and by mounts stained with carbol fuchsin, Gram's stain, and nigrosine.

CARBOHYDRATES. A sample of the mash was clarified with lead acetate deleaded with sodium carbonate, and reducing sugars (expressed as glucose) were determined by the Shaffer and Hartmann method (17). This procedure gives slightly too high results because small quantities of acetylmethyl carbinol and other reducing bodies, which are formed in the fermentation, are calculated as glucose. Starch was determined by the acid-hydrolysis method, and pentosans by distillation with hydrochloric acid.

THE BACTERIOLOGICAL and chemical changes which occur in the fermentation of corn mash by the acetone–butyl alcohol organism, Clostridium acetobutylicum, have been determined at short intervals throughout the fermentation.

The vegetative cells were the active agents of fermentation, and during the period of greatest activity transformed more than one-half of their weight of starch into gases, acids, and solvents every hour.

Concurrently with the fermentation of the starch occurred a rapid and extensive hydrolysis of the corn proteins. About two-thirds of the insoluble protein was converted into soluble products, such as proteins, proteoses, peptones, and amino acids.

ACIDS. The pH value of the mash was determined colorimetrically on a sample diluted with carbon dioxide–free water and filtered before taking the reading. Titratable acid was obtained by diluting 10 cc. of sample with an equal volume of water, heating to boiling, and titrating with 0.1 *N* sodium hydroxide and phenolphthalein. The volatile acid in either a 250-cc. or a 500-cc. sample was removed by acidifying with sulfuric acid and distilling with steam. The distillate was refluxed to get rid of carbon dioxide and titrated to phenolphthalein with 0.1 *N* barium hydroxide. After evaporating the neutralized distillate to a small volume, the acids in an aliquot were set free with sulfuric acid and subjected to a Duclaux distillation. From the Duclaux data the percentages of acetic and butyric acids were calculated by the method of Gillespie and Walters (6). The residue from the volatile-acid distillation was evaporated to about 100 cc., and the nonvolatile acid extracted with ether and titrated.

SOLVENTS. Fifteen hundred cubic centimeters of mash were distilled, and the total solvents determined from the specific gravity of the distillate. In the distillate, acetone was determined by Goodwin's modification (7) of the Messinger method, ethyl alcohol by Bogin's water-titration method (1), and butyl alcohol by difference. Acetone was determined in all the samples, but, owing to the fact that the methods do not measure very small quantities of total solvents and ethyl alcohol, these were not determined until the twenty-first hour after inoculation.

NITROGEN. Samples of 25 cc. capacity were analyzed for total nitrogen by the Kjeldahl method. The mash was filtered through paper pulp, and the soluble nitrogen determined in a 50-cc. sample. Fifty cubic centimeters of the filtrate were evaporated at a low temperature to 20 cc. and then made to 25 cc., and 5- or 10-cc. aliquots used for the determination of amino nitrogen with the Van Slyke apparatus. In another aliquot the proteins were precipitated by the Folin and Wu tungstic acid method (4). After filtering, a portion of the filtrate was analyzed by the Kjeldahl method for non-protein nitrogen. The soluble protein nitrogen was obtained by difference between the total soluble and the non-protein nitrogen.

RATE OF GROWTH OF *Clostridium acetobutylicum* IN CORN MASH

In the first experiment the initial number of bacteria was approximately 6 million per cubic centimeter. At intervals of 3 hours during the early stages, and later at longer intervals, samples were drawn and analyzed as shown in Figure 1. Because of the large inoculum ratio, 1 to 40, it was to be expected that the bacteria would develop without displaying much of the usual lag period. Actual measurements of the total numbers of bacteria were in agreement with this supposition. The number of cells followed a logarithmic curve during the early period of growth until the conditions became such that growth was retarded, and the rate of increase began to decline. Since acid production is widely used as a guide to the progress of fermentation, the chart includes titratable acidity at different periods of fermentation. The time required for reduction of methylene blue is also included. Because of the good preparations and the consequent ease of examination, the total counts and also the clostridial counts were made from the Gram stains. *Cl. acetobutylicum* is Gram positive at first, and in the later stages of growth Gram negative—e. g., after 75 hours, less than 5 per cent of the total number of cells were Gram positive.

If the curves for titratable acid and number of bacteria are compared, it will be seen that up to the fifteenth hour the two are approximately parallel. Later they become quite divergent; the acidity falls rapidly after the eighteenth hour, while the number of bacteria does not fall off appreciably until after the thirty-third hour. The period between the eighteenth and thirty-sixth hours is the most active of the entire fermentation. This is the time during which starch destruction and solvents production are most rapid. It is evident from a comparison of the bacteriological and chemical data that the vegetative cells are the forms which bring about the chemical changes in the medium. There is a fairly close relationship between numbers of vegetative cells (called bacteria in the figure), hydrolysis of starch and protein, and formation of acids, solvents, and other products. No apparent relationship exists between numbers of clostridia and formation of products.

The reduction of methylene blue is much more intimately related to the number of bacteria than is the acidity; the greater the number of cells, the shorter is the time of reduction. The minimum time needed for reduction occurs at

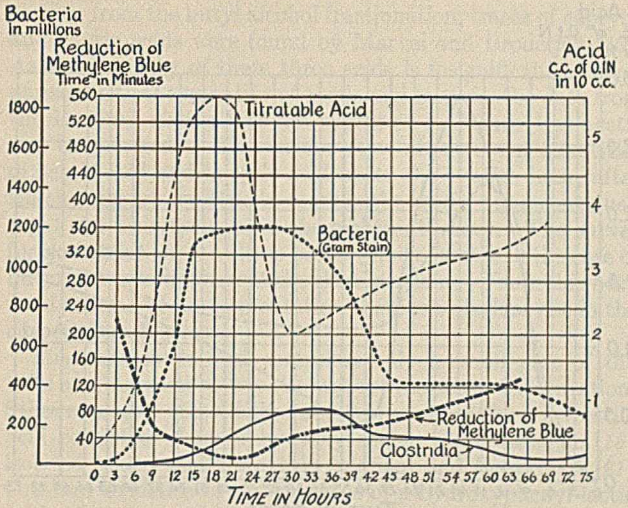

FIGURE 1. NUMBER OF BACTERIA, TIME OF REDUCTION OF METHYLENE BLUE, AND ACID PRODUCTION AT DIFFERENT STAGES DURING FERMENTATION

(Experiment 1)

about the same time as the peak in numbers of cells, but the reducing agent continues active long after the total number of cells has begun to decline.

Hanging-drop mounts showed merely that the cells of the young culture are actively motile; later, when the products begin to accumulate, there is a marked decline in number of motile organisms. After 36 hours the cells are all non-motile.

One of the most interesting points recorded in Figure 1 is the rate of formation of the spindle-shaped forms, or clostridia. These forms, so characteristic of the butyric acid bacteria, give the granulose reaction with iodine, and were first noted when the culture was 6 to 9 hours old, and reached a maximum at 30 to 36 hours. Thereafter the number of clostridia decreased. As indicated in a previous report (*11*), this decrease in numbers of clostridia is associated with the liberation of free spores.

The results from the dilution counts (not given in the figures) were extremely irregular and were only from one-tenth to one-hundredth as high as the direct counts. Two reasons for this are suggested. First, the direct count includes many dead or inactive cells which naturally do not appear in the dilution count. Second, the dilution count tends to give figures even lower than the actual number of viable cells; it is highly probable that the associated action of several cells is necessary to insure an environment suitable for reproduction.

LIFE CYCLE OF THE ORGANISM. A study of the cyclical changes in the development of *Cl. acetobutylicum* throughout the fermentation included observations of the size, shape, characteristics of grouping, and variation in staining of the cells. The young, vigorous, rapidly dividing, rod forms found at the beginning of the maximum growth phase are enormous in length (4.7μ) but not unusual in width (0.72 μ). As the culture grows older and passes the phase of maximum numbers, from 27 to 30 hours after inoculation, there is a decrease in size. The average is now about 3.7μ long and 0.66μ wide. A large number of club-shaped cells (clostridia) are present and are somewhat larger (4.7μ × 1.6 μ) than the vegetative cells. Many cells are grouped parallel to one another as rafts or in typical echelon formations. At 60 to 70 hours of age the vegetative cells have decreased still farther in size (2.6 μ × 0.6 μ), the clostridia have passed their maximum number, and many spores have appeared. The spores are oval bodies about 2.4 μ long and 1.2 μ wide. The chains and echelon formations have entirely disappeared at this time. After 60 to 70 hours the cells do not take the stain so easily as before and show many irregular forms.

RATE OF BACTERIAL METABOLISM. Assuming that 1000 million bacteria weigh 1 mg. (the figure commonly used for soil forms which are smaller than *Cl. acetobutylicum*), the count of 1200 million per cubic centimeter would be equivalent to 1.2 mg. of cells per cubic centimeter, or 1.2 grams per liter. During the period of most rapid chemical change (18 to 30 hours), 10 grams per liter of starch were destroyed. Assuming that this is all converted into gas, solvents, etc., 1 gram of bacteria metabolizes about 0.7 gram of starch per hour. This tremendous rate of metabolism gives an idea of the enormous power of transforming matter possessed by these bacteria.

CHEMICAL CHANGES

The principal chemical changes noted in the first experiment are represented graphically in Figures 2 and 3, and will be discussed in the following paragraphs.

CARBOHYDRATES. The starch decreased progressively throughout the fermentation, but most of the change was completed at the end of 50 hours. The reducing sugar reached a maximum at 42 hours and then fell off rapidly to the end. The curve of the latter measures the difference between production and consumption and necessarily does not follow the destruction of starch. The quantity of starch hydrolyzed during the rise in sugar concentration averages more than four times the quantity of sugar that is observed. The pentosan content of the medium showed little or no change throughout the fermentation. Pentosans are apparently not attacked by *Cl. acetobutylicum*.

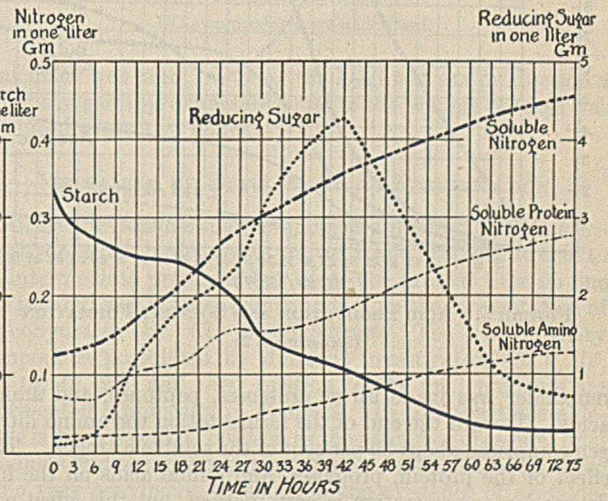

FIGURE 2. CHANGES IN CARBOHYDRATES AND FORMS OF NITROGEN CAUSED BY *Cl. acetobutylicum*

(Experiment 1)

FORMS OF NITROGEN. It is probable that digestion of protein plays an important role in the fermentation, and is just as much a part of the life of the bacteria as the destruction of carbohydrates. The extent of proteolysis by *Cl. acetobutylicum* is equal to that brought about by many distinctly proteolytic bacteria. The process is regular and continuous, and proceeds concurrently with the fermentation of the carbohydrates. At about 54 hours the soluble and insoluble nitrogen were equal, and at the end of 75 hours about 60 per cent of the total nitrogen (0.8 gram per liter) was in the soluble condition.

An examination of this nitrogen shows that proteolysis resulted in a large number of cleavage products. About 60 per cent of these were in the form of soluble protein, and the

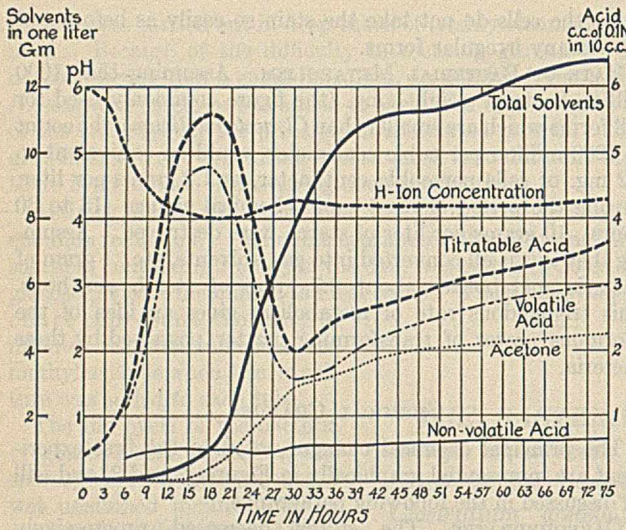

FIGURE 3. ACID PRODUCTION AND SOLVENT FORMATION
(Experiment 1)

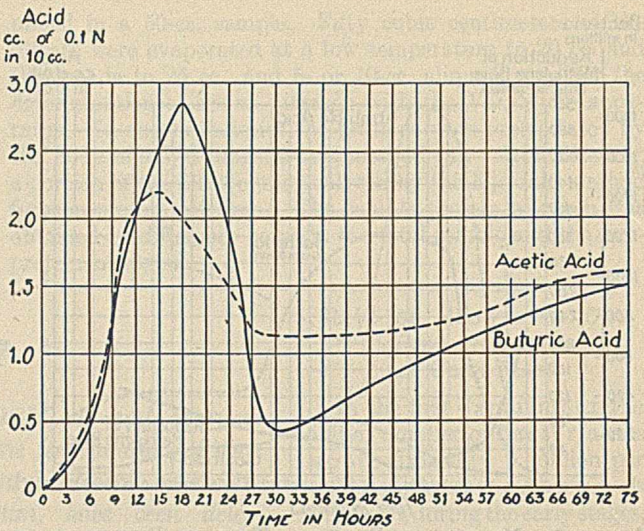

FIGURE 4. NATURE OF VOLATILE ACIDS FORMED BY *Cl. acetobutylicum*
(Experiment 1)

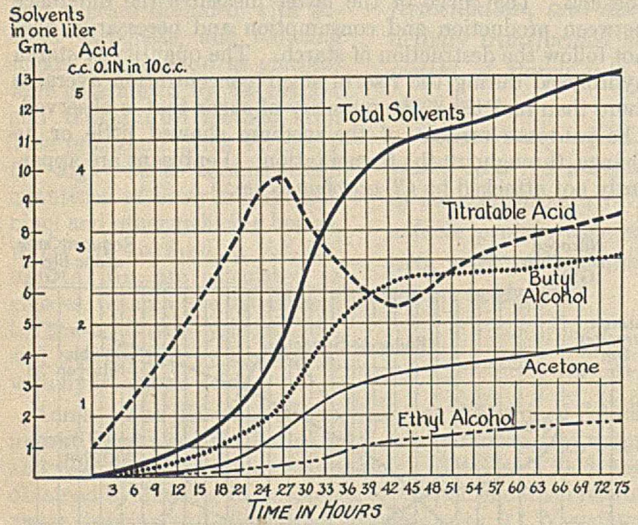

FIGURE 5. ACID PRODUCTION AND SOLVENT FORMATION
(Experiment 2)

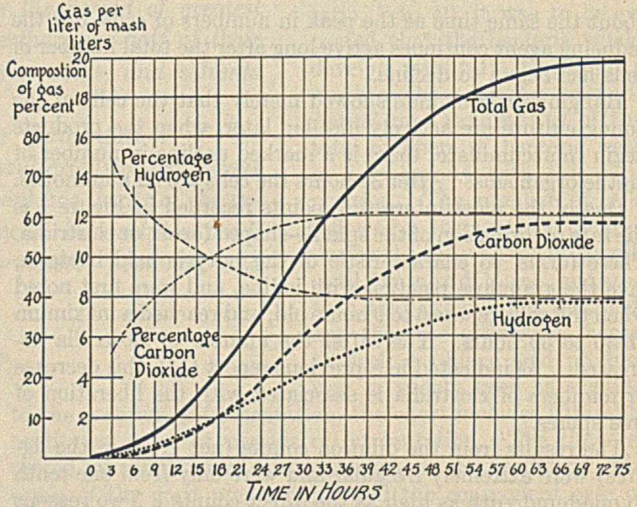

FIGURE 6. PRODUCTION OF GAS IN BUTYL ALCOHOL FERMENTATION
(Experiment 3)

remainder was made up of proteoses, peptones, and amino acids. Toward the end of the fermentation the amino nitrogen comprised about 30 per cent of the soluble nitrogen. The effect of the protein, proteoses, and amino acids on the hydrogen-ion concentration is very marked, but this effect will be discussed in connection with the production of acids.

ACID AND SOLVENT PRODUCTION. The curves of titratable acid and volatile acid run almost parallel throughout the fermentation. The nonvolatile is about equal to the difference between the titratable and the volatile. The peak in acidity came at the end of 18 hours, and then the curve broke sharply until the thirtieth hour, when the second slow rise began and continued to the end of the fermentation. Solvents production became rapid at the time of maximum acidity and continued at a high rate until the forty-second hour. From the eighteenth to the thirtieth hour, consumption of acid exceeded its production, and a drop in acidity occurred. It is quite evident, however, that a much larger quantity of acid has been consumed than is indicated by the decrease. During these 12 hours there were produced about 7.0 grams per liter of solvents containing approximately 2.1 grams acetone and 4.2 grams butyl alcohol. The acid equivalent of these solvents calculated from Figure 7, is 9.1 grams. During the same time, the titratable acid decreased only about 2.5–3.0 grams per liter. It therefore seems evident that approximately 6 grams per liter of acid must have been produced in addition to that which was already present when the break began. It is probable that from the eighteenth to the thirtieth hour the acid production is at least twice and perhaps four times as great as during the rapid rise of the curve from the sixth to the twelfth hour. If this view is correct, the period of greatest acid production is during the fall of the acid curve. After the thirtieth hour, acid production again outruns conversion into solvents, and a rise in the curve takes place.

The hydrogen-ion concentration in a general way reflects the changes in titratable acid, but the fluctuations are much less marked because of the buffer action of the proteolytic products.

NATURE OF ACIDS. Reilly et al. (*14*), Speakman (*18*, *20*), Donker (*3*), Stiles et al. (*22*), and Van der Lek (*23*) have shown that the volatile acid consists almost entirely of acetic and butyric acids. Traces of formic acid have been reported by Donker (*3*), and Stiles et al. (*22*), and, in the "yellow oil" residue from the butyl alcohol fractionation, traces of caprylic and capric acids were found by Marvel and Broderick (*10*). As the quantity of these three acids is insignificant in comparison with the quantity of acetic and butyric, the data from the Duclaux distillations are expressed in Figure 4 as acetic and butyric only. The curves show about equal quantities of acetic acid and butyric acid up to the twelfth hour, after which there is very little increase in the acetic, but a continued rapid rise in butyric, until the eighteenth hour. The curves for both acids show a sharp break (much greater in the case of butyric) to a minimum at the thirtieth hour. From this hour until the end of the fermentation there is a gradual rise in the curves of both acids.

The nonvolatile acid comprises only a small part of the total and increases slowly throughout the entire fermentation. Stiles et al. (*22*) showed that about one-half of the nonvolatile acid consisted of alpha-hydroxy acids. Schmidt et al. (*15*) isolated leucic acid from this fraction, and Speakman (*21*) obtained evidence of the presence of *p*-hydroxyphenyl-lactic acid. It is probable that some of the nonvolatile acid arises, not from carbohydrate decomposition, but from deamination of amino acids.

INTERRELATION OF VARIOUS SOLVENTS. Owing to the fact that the data for ethyl alcohol in the first experiment were incomplete, a second experiment was carried through for the production of solvents. The first sample was taken at the end of 21 hours, about as early as ethyl alcohol can be determined. Five liters of mash were taken for the first two samples, 4 liters for the next three, and 2 liters for the others. With such large samples it was possible by successive distillations to concentrate the solvents to such an extent that ethyl alcohol could be determined by the water-titration method. The data are given in Figure 5. This fermentation proved to be somewhat slower than that of the first experiment. Titratable acidity rose more gradually, and the production of solvents was slower, but the final yield of solvents was 0.5 gram per liter more than in the first experiment. As compared with former results (*22*, *24*), the total solvents show an unusually high proportion of ethyl alcohol (13 per cent) and a low content of butyl alcohol (54 per cent). The average figures for the various solvents have been: acetone, 31 per cent; ethyl alcohol, 9 per cent; and butyl alcohol, 60 per cent. The three solvents—acetone, ethyl alcohol, and butyl alcohol—were produced simultaneously throughout the fermentation, but certain periods were characterized more definitely by the production of one or more of the three compounds. Sweeping generalizations cannot be made, but the data as a whole point to a period of high acidity as a period of high acetone-production. In the low part of the acidity curve the production of acetone is low, and that of butyl alcohol is high. It is probable that the hydrogen-ion concentration affects the production of these two solvents in an opposite manner. In this connection, attention is called to the marked lowering of the acetone-solvents ratio when the fermentation takes place in the presence of an excess of calcium carbonate (*22*, *25*).

PRODUCTION AND COMPOSITION OF GAS. It has been generally reported (*14*, *19*) that, in the early stages of fermentation, hydrogen is the chief gas produced.

The data reported in Figure 6 were obtained from a flask containing 300 cc. of mash which filled the flask to the neck and left only about 20 cc. of unoccupied space above the mash. The gas was collected over mercury in an apparatus somewhat similar to that devised by Harden, Thompson, and Young (*8*), and analyzed in a Burrell apparatus. The gas collected at the end of 3 hours was entirely hydrogen, because all the carbon dioxide produced up to this time was absorbed by the medium. When the flask was boiled for several minutes, 13.5 cc. of hydrogen and 27 cc. of carbon dioxide were driven out of solution.

The remaining gas samples were collected from an unboiled duplicate culture. As the fermentation proceeded, the percentage of hydrogen decreased. Up to the eighteenth hour the volume of hydrogen exceeded that of carbon dioxide, but, from then on, the volume of the latter was larger. The time of rapid rise in carbon dioxide evolution was coincident with the fall of acidity and the production of solvents. Of the total volume of gas, about 60 per cent was carbon dioxide and 40 per cent hydrogen. The total volume of gas was almost twenty times the volume of mash. This varies of course with the concentration of the mash. In this experiment a 6 per cent mash was used. During the height of gas production a volume of gas approximately equal to the volume of mash was produced every two hours.

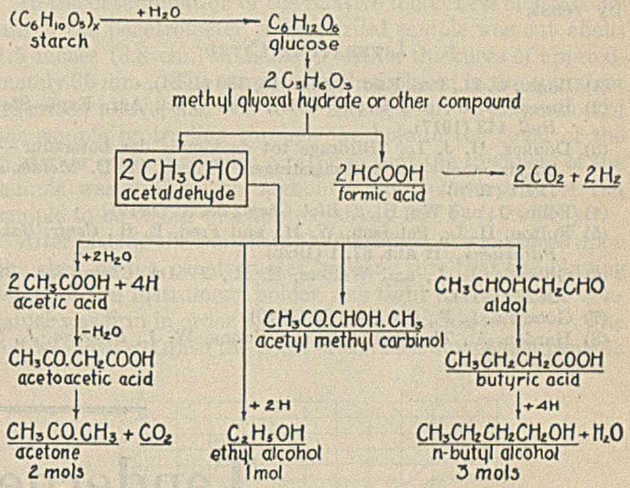

FIGURE 7. DEGRADATION OF CARBOHYDRATES BY *Cl. acetobutylicum*

(Known products are underlined)

MECHANISM OF BUTYL-ACETONIC FERMENTATION

All theories assume such compounds as methyl glyoxal, acetaldehyde, aldol, hydroxy-butyric acid, and acetoacetic acid to be intermediate products, but up to the present time no one has isolated any of these compounds from the fermentation of carbohydrates by *Cl. acetobutylicum*. The intermediary compounds postulated by different investigators (*3*, *9*, *12*, *14*, *16*, *19*, *20*), and their relation to the final products are represented graphically in Figure 7. In this chart acetaldehyde is given a central position as the precursor of several final products and the intermediary product, aldol, although there is no very convincing evidence of the existence of acetaldehyde. Neuberg and Arinstein (*12*) isolated it from the fermentation of carbohydrate by a related microörganism, *B. butylicus* (Fitz), but the findings of these authors do not necessarily apply to *Cl. acetobutylicum*. The present authors have tried many methods for the fixation of acetaldehyde, such as addition of sodium or calcium sulfite, dimethylhydroresorcinol, and charcoal, but, while there has been no difficulty in obtaining acetaldehyde from other fermentations, no trace of it has been obtained from the acetone–butyl alcohol fermentation.

It is probable that if the fermentation were carried on in the presence of a neutralizing agent (e. g., calcium carbonate), much valuable evidence that is masked by the secondary and superimposed process—namely, the production of solvents—would be revealed. It is quite possible that under such conditions the existence of methyl glyoxal, acetoacetic acid, hydroxy-butyric acid, or other intermediate compounds could be established. Other lines of attack, such as the addition of assumed intermediates to the actively fermenting culture, or studies with enzymes from the bacterial cell, might also prove exceedingly fruitful.

The solvents formed in the fermentation of corn mash have been calculated to molar quantities and are given in Figure 7. They appear in approximately the proportions: 1 mole C_2H_5OH, 2 moles $CH_3CO{\cdot}CH_3$, 3 moles C_4H_9OH. There are apparently no reasons per se why these molar relations should exist, and why they are so resistant to change. Perhaps if a better understanding of the mechanism of the fermentation were available, it would be possible to modify the proportions of the products as has been done in the production of glycerol by yeast.

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Tenderness of Meat

I. Determination of Relative Tenderness of Chilled and Quick-Frozen Beef

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TWO NOVEL METHODS for estimating the relative tenderness of meat are compared. One of these methods involves the use of an instrument constructed from an ordinary tire-pressure gage. The other instrument is a modified New York Testing Laboratory standard penetrometer. The relative tenderness of various cuts of beef of several grades is indicated. The effect of quick-freezing on the tenderness of beefsteak has also been determined and is presented in tabular form. These data indicate that after quick-frozen meat has been stored for one week, it is approximately 20 per cent more tender than before freezing.

MUCH work on the relationship of the connective-tissue content and the relative tenderness of meats has been done by Mitchell, Zimmerman, and Hamilton (*2*) and by Mitchell, Hamilton, and Haines (*1*). While this work may be of value in indicating the age of the animal when slaughtered and the care given it prior to slaughtering, the results cannot be considered absolute. It is a generally recognized fact that pounding or hammering tenders meat. Many persons instruct the butcher selling the meat to hammer their steaks immediately after cutting. Some cooks always hammer the meat just prior to cooking. The hammering of the meat changes it physically so that it is more easily masticated, but this probably has little chemical effect on it. It is doubtful that a determination of the amounts of collagen and elastin in the muscle tissue, as carried out by Mitchell and his co-workers, would indicate any change in the meat because of the hammering process.

Preliminary comparative tests of the eating qualities of samples of meat were unsatisfactory because of the inability to obtain in some cases an agreement of the testers concerning the relative tenderness of any particular sample. Moreover, difficulties were encountered in obtaining uniform cooking of the samples. Chewing tests were found to be of value only when a wide difference in the tenderness of the meat existed.

A mechanical device for determining the shearing strength of meat (the so-called mouse trap) was developed in the laboratory at Beltsville by Baker and reported by Warner (*5*).

The work reported by Warner and Baker is not a direct comparison of tough and tender meats but is a study of the correlation between the breaking strength of the meat muscles of the left and right side of a given animal and a similar comparison of the shearing strength of raw and cooked meat.

As yet the results obtained by the devices described in this paper have not been compared with those which may be obtained by means of their apparatus for determining the shearing or breaking strength of meat, but this will be done and reported in a later article.

It is often stated that the quick-freezing of meat noticeably tenders it, but no one has carried out chemical or physical tests to prove the point. In this case it is very unlikely that any chemical method could be developed which would indicate changes in tenderness in the meat during freezing. No one has as yet demonstrated exactly how quick-freezing of meat tenders it, but certain investigators have postulated that

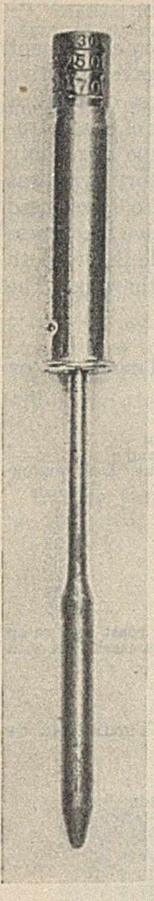

Figure 1. Cutting Gage

this effect is caused by the stretching of the partially frozen connective tissue during the expansion of the meat on freezing. Such a change is a physical phenomenon not determinable chemically.

Therefore, when a study of the effect of quick-freezing on the tenderness of meat was proposed, it became necessary to study mechanical means of estimating the relative tenderness of meat before and after freezing. Since the method developed had to be directly comparable to a chewing test, the two procedures which were tried were based on the measurement of simple cutting and penetration operations. One method involves the estimation of the force required to cut or puncture the meat with a blunt instrument. This test is comparable to cutting meat with the teeth. The other method proposed is in reality a test of the depth a blunt instrument, pressed down with a given weight for a definite time, will penetrate into a piece of meat confined in a given space. This procedure is comparable to an estimation of the depth which the teeth, impelled with a given muscular effort, will penetrate into a piece of meat.

Apparatus Used

Cutting Gage. The cutting or puncturing apparatus (Figure 1) consists of an ordinary Schrader tire-pressure gage having a blunt instrument inserted in it. The puncturing or cutting part of the instrument is 2.5 inches long and $^5/_{16}$ inch in diameter. The end is symmetrically tapered to a cone approximately $^3/_8$ inch in height and an angle of 13°. The point which is rounded has a radius of approximately 0.08 inch. A clamp, similar to a tennis-racket press, was constructed for holding the meat in place so that it did not rest on the table.

In order to determine the relative tenderness of meats by the use of this instrument, a piece of meat 3 inches square by 1 inch thick was placed between the perforated plates of the press. The wing nuts were then screwed down tightly, thus closing the press and holding the sample securely. The press was placed in a vertical position and the cutting-gage instrument was pushed through the meat in the press. As the gage passed through the meat, the indicator registered the pressure required to force it through. There are eight holes in the plates of the press, through each of which the instrument was pushed, thus obtaining eight readings. These readings were averaged in order to obtain the recorded figure. The Schrader tire gage is constructed for measuring air pressure and does not indicate the actual pressure exerted on the meat in order to push the instrument through it; thus it was necessary to convert the readings obtained to pounds pressure exerted on the meat. The particular Schrader instrument used was calibrated for actual pounds pressure exerted, as is indicated in Figure 2. The curve obtained was used in converting the instrument readings to actual pounds pressure required to puncture. These data are presented in Tables I and II.

Penetrometer. The penetrometer (Figure 3) used in determining the relative tenderness of meat is of the New York Testing Laboratory standard type for determining the consistency of bituminous materials (*3*, *4*). A new blunt instrument to replace the Robert No. 2 needle as used with the penetrometer was designed to give a comparison between tough and tender meat. The new instrument or needle (Figure 3) used in carrying out these tests was $1^3/_8$ inches long, having a diameter of 0.15 inch and a rounded point with a radius of approximately 0.07 inch.

A shallow cylindrical container about 15 inches in diameter and approximately 1 inch in height fitted with a screw cover was used as a container for the meat sample. The cover of this container had a hole $^3/_8$ inch in diameter through which the penetration instrument passed. A 255-gram weight was used to force the penetration instrument into the meat.

In the determination of the relative tenderness of steaks by use of the penetrometer, a cylindrical sample was cut about 1.5 inches (3.8 cm.) in diameter with a thickness of approximately 30 mm. The sample was then placed in the container described above, and the cover screwed on. The portion of the sample protruding through the hole in the cover of the container was cut off with a razor so that the thickness of the sample was uniform throughout. The temperature of the sample to be tested was approximately 60° F. (15.6° C.)

After placing the sample in the container, it was placed upon the shelf of the penetrometer, making sure that the binding screw of the instrument holder was tight and that the container was firm in order to prevent any rocking motion. The rod was lowered until the point of the instrument just came in contact with the surface of the sample. This could best be done by observing the reflection of the point of the instrument and the surface of the meat in the mirror attached to the apparatus.

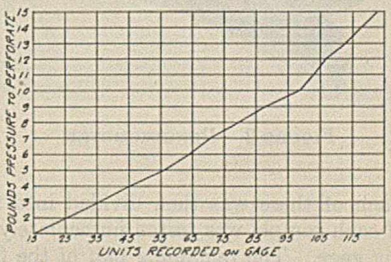

Figure 2. Calibration of Cutting Gage

After setting the needle, the counterweight was slowly moved down until the foot of the rack rested on the head of the rod, and the reading on the dial was taken. With one hand the clamp was opened by pressing the button, and with the other hand the chronometer was started. At the end of exactly 15 seconds the clamp was released, the rack lowered to the top of the rod, and the reading on the dial again taken. The difference between the first and second readings in tenths of a millimeter was the penetration under the above conditions. As many uniform samples as could be cut from each steak were tested. The smaller steaks yielded only three, but the larger ones gave enough samples for six or seven penetration tests. The average variation in the individual tests was ±2.0 mm.

Preliminary Experiments

The perforating or puncturing instrument constructed from the Schrader tire-pressure gage was suggested by Dean A. Pack as a suitable instrument for determining the amount of pressure required to force a cutting or puncturing implement through a sample of meat of given thickness. This instrument was given a preliminary test on a uniform sample of bottom of the round steak from a Grade C heifer. In this test the steak was cut into three samples as nearly uniform as

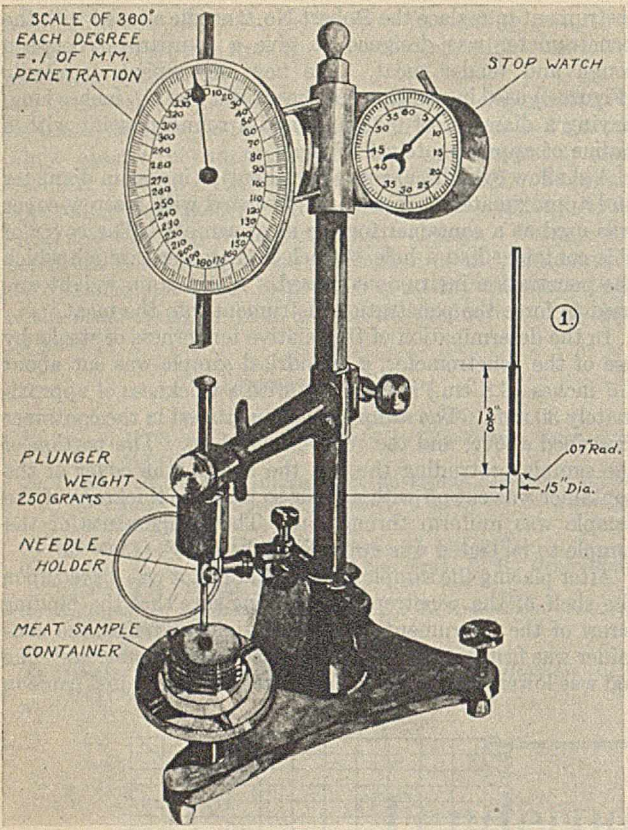

FIGURE 3. PENETROMETER

possible. Each of these was then divided into two pieces. One piece of each sample was tested immediately by means of the cutting gage. The remaining half of the first sample was quick-frozen in a Birdseye multiple plate froster and then quickly thawed and tested by means of this instrument. The second sample was frozen in the same manner as the first and stored at −20° F. (−28.9° C.) for 9 days and then thawed and tested. The third steak sample was frozen in the same manner as the first two and then stored at the same temperature as the second for 16 days; after thawing, its relative tenderness was determined. The results of these tests are indicated in Table I.

TABLE I. EFFECT OF QUICK-FREEZING ON TENDERING OF STEAK[a]

(Determined by cutting gage)

STEAK SAMPLE	TREATMENT	STORAGE[b]	PRESSURE TO PERFORATE	DIFFERENCE
		Days	*Pounds*	*Pounds*
1	Unfrozen	0	8.4	
1	Quick-frozen	Tested immediately after freezing and thawing	7.55	0.85
2	Unfrozen	0	7.65	
2	Quick-frozen	9	5.68	1.97
3	Unfrozen	0	9.3	
3	Quick-frozen	16	5.28	4.02

[a] Bottom of round steaks from Grade C heifer.
[b] Storage temperature −20° F. (−28.9° C.).

The results of this preliminary experiment indicate that the quick-freezing operation reduces considerably the pressure required to perforate the meat with the puncturing instrument. Moreover, there is a progressive tendering during storage, the relative tenderness increasing even more during storage than on quick-freezing.

RELATIVE TENDERNESS OF VARIOUS CUTS OF STEAK

Although the results obtained in the preliminary experiment described above indicated that the cutting gage gave a positive measure of the relative tenderness of two pieces of meat, a method of checking the results obtained by means of this instrument was needed. A penetrometer of the type commonly referred to as the New York Testing Laboratory type was obtained. This instrument, illustrated in Figure 3, was used as described above in a comparison of the relative tenderness of various cuts of steak from one half of a Grade B cow, both before and after quick-freezing and subsequent thawing. The results are presented in Tables II and III.

TABLE II. EFFECT OF QUICK-FREEZING ON TENDERING OF GRADE B BEEF[a]

(Determined by cutting gage)

SAMPLE	PRESSURE TO PERFORATE		DIFFERENCE
	Unfrozen	Quick-frozen and stored 1 week[b]	
	Pounds	*Pounds*	*Pounds*
Sirloin steak	3.1	2.0	1.1
Back of rump	3.86	2.7	1.16
Face of rump	6.4	4.08	2.32
Bottom of round	15.1	7.14	7.96
Pot roast from bottom round	9.8	8.52	1.28
Top of round steak	7.02	5.4	1.62
Pot roast from top round	8.11	7.55	0.56

[a] Because of the lack of sufficient samples of sirloin roast and rump tenderloin from this half cow, no tests on these cuts were carried on with the cutting gage.
[b] Storage temperature −20° F. (−28.9° C.).

TABLE III. EFFECT OF QUICK-FREEZING ON TENDERING OF GRADE B BEEF

(Determined by penetrometer)

STEAK	PENETRATION	
	Unfrozen	Quick-frozen and stored 1 week[a]
	Mm.	*Mm.*
Sirloin roast	16.9	19.7
Sirloin steak	16.3	17.6
Rump tenderloin	22.2	26.9
Back of rump	15.0	19.1
Rump steak	19.4	18.9
Face of rump	11.4	15.4
Pot roast from top round	11.1	14.2
Pot roast from bottom round	10.8	12.8
Top of round steak	11.3	15.2

[a] Storage temperature −20° F. (−28.9° C.).

The data obtained by the use of both of these instruments indicate that the various cuts of steak differ in relative tenderness in about the proportion ordinarily assumed. Thus, bottom of the round steak was shown to be much tougher than that obtained from the top of the round. Top of the round, in turn, was tougher than rump and sirloin steak. Rump and rump tenderloin were more tender than any of the other steaks.

In all but one test there was a material tendering effect caused by quick-freezing and storing at low temperature for a week. On the average this was approximately 20 per cent.

EFFECT OF COLD STORAGE ON TENDERNESS OF MEAT

Since the preliminary test of the effect of quick-freezing on the tendering of meats indicated an actual increase in the relative tenderness of meat during a short period of storage, other storage tests of meat have been begun. These tests have not as yet been completed but the result of one experiment which has been carried as far as 5 weeks is presented in Table IV.

TABLE IV. EFFECT OF QUICK-FREEZING AND STORAGE[a] ON TENDERNESS OF GRADE A AND GRADE C SIRLOIN BEEFSTEAKS

GRADE A	GRADE C	REMARKS
Mm.	*Mm.*	
22.7	16.4	Unfrozen
25.0	17.6	Quick-frozen and stored 1 week
25.9	22.2	Quick-frozen and stored 3 weeks
27.7	23.4	Quick-frozen and stored 5 weeks

[a] Storage temperature −20° F. (−28.9° C.).

In this experiment the penetrometer was used as the instrument to determine the relative tenderness. The effects of storage on a Grade A and on a Grade C sirloin steak were compared. The data indicate that there was a gradual increase in tendering both grades of meat for the period of the experiment, and that the tendering effect was more pronounced in the case of the tougher (Grade C) steak than in the Grade A sirloin steak. It is noteworthy that the Grade C steak after 5 weeks' storage was as tender as the Grade A sirloin steak prior to freezing.

This experiment is a preliminary one, and the result, although exceedingly interesting, should not be considered as absolutely conclusive evidence that a low grade of steak may be made as tender as a high-grade steak by quick-freezing and holding in cold storage. Further work is under way and will be reported at a later date.

CONCLUSIONS

1. The two mechanical means of determining the relative tenderness of meat suggested in this paper are sufficiently sensitive to indicate that there is a great difference in the tenderness of various cuts of fresh unfrozen beef obtained from the same animal carcass; these are, therefore, reliable for measuring the relative tenderness of other cuts of meat.

2. Quick-freezing of meat and the subsequent storage of the frozen product effects a marked tendering of the beef.

The tendering of quick-frozen meat continues during cold storage.

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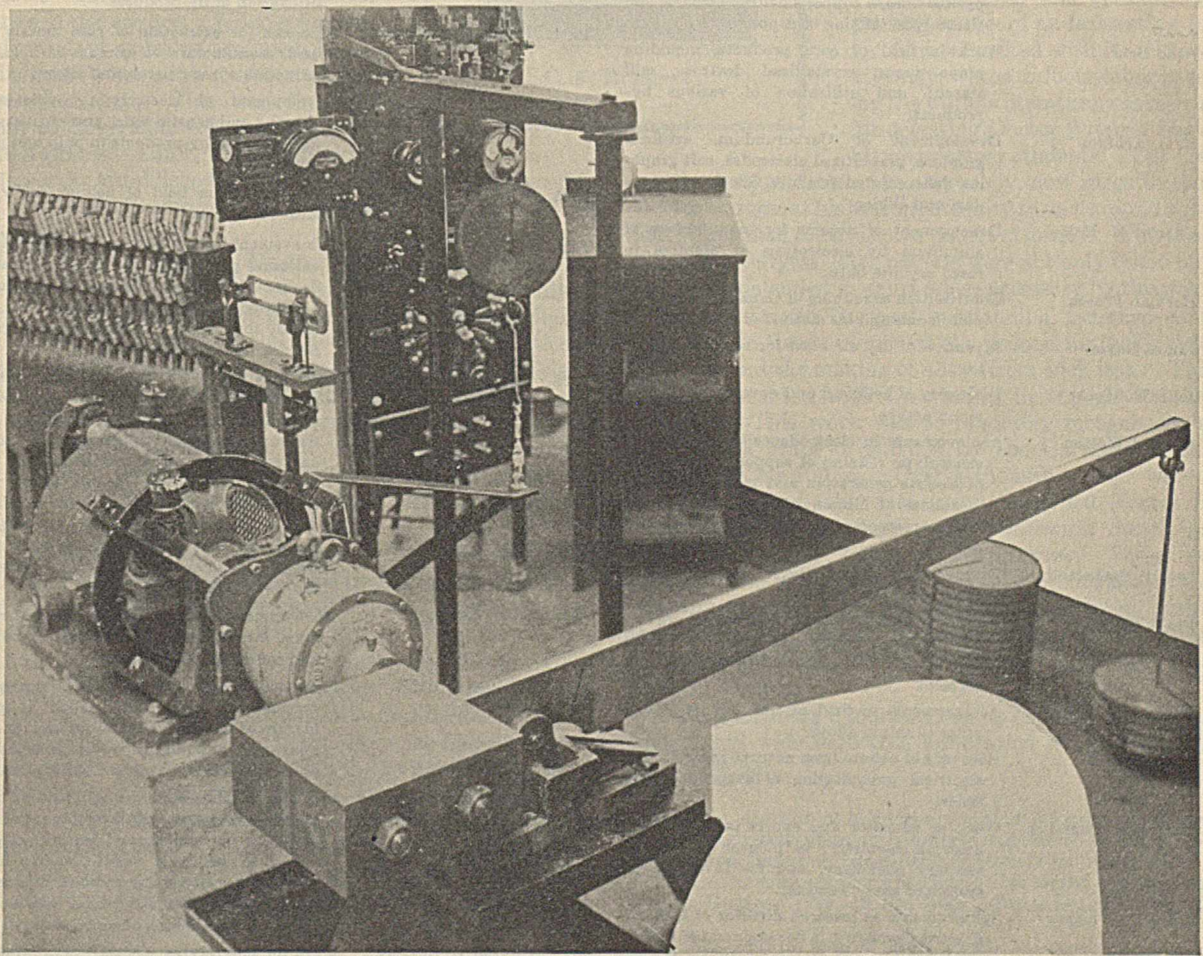


Courtesy Standard Oil Development Co.

MOUGEY PIN AND BUSHING TEST APPARATUS. USED TO DETERMINE LOAD-CARRYING CAPACITY OF LUBRICANTS

PERKIN MEDAL AWARD

THE Perkin Medal for 1932 was presented to Charles F. Burgess, president of C. F. Burgess Laboratories, Inc., 202 East Forty-fourth Street, New York, on January 8, at the joint meeting of the American Section of the Society of Chemical Industry, the AMERICAN CHEMICAL SOCIETY, the Société de Chimie Industrielle, and the American Electrochemical Society in New York City.

Howard F. Weiss, of New York, described the accomplishments of the medalist, followed by the presentation of the medal by Marston T. Bogert of Columbia University, and the address by the medalist himself. Allen Rogers, of Pratt Institute, chairman of the American Section, presided.

The Perkin Medal may be awarded annually by the American Section of the Society of Chemical Industry for the most valuable work in applied chemistry. The award may be made to any chemist residing in the United States of America for work which he has done at any time during his career, whether this work proved successful at the time of execution or publication, or whether it became valuable in subsequent development of the industry. The medalist is chosen by a committee representing this society, the AMERICAN CHEMICAL SOCIETY, the American Electrochemical Society, the American Institute of Chemical Engineers, and the Société de Chimie Industrielle. It was founded in 1906 by Sir William H. Perkin, the first medal being presented to Sir William himself.

* * *

PERKIN MEDAL AWARDS

DATE	AWARDED TO	PRINCIPAL ACHIEVEMENTS
1906	Sir William H. Perkin	Pioneer work in synthetic dye industry.
1908	J. B. F. Herreshoff	Improvements in chamber process for sulfuric acid; development of the contact process for sulfuric acid, a roasting furnace for pyrites fines, a copper smelting furnace, and electrolytic refining of copper.
1909	Arno Behr	Work in field of corn products, including grape sugar, crystallized dextrose, mill starch; and utilization of various by-products.
1910	E. G. Acheson	Development of Carborundum, artificial graphite, graphitized electrodes, soft graphite, deflocculated graphite, Siloxicon, Aquadag, and Oildag.
1911	Charles M. Hall	Development of process for manufacture of aluminum by electrolysis of alumina in fused cryolite bath.
1912	Herman Frasch	Contribution to refining of Canadian and Ohio petroleums and his method of mining sulfur.
1913	James Gayley	Invention of dry air blast for manufacture of iron.
1914	John W. Hyatt	Discovery of celluloid and development of its manufacture.
1915	Edward Weston	Achievements in electrodeposition of metals, electrolytic refining of copper, construction of electric generators and motors, arc and incandescent illumination, electric measuring instruments, and the Weston standard cell.
1916	Leo H. Baekeland	Discovery of Velox paper, Bakelite, and of other synthetic resins.
1917	Ernst Twitchell	Discovery and development of use of organic sulfo acids as catalysts in hydrolysis of oils and fats for production of fatty acids and glycerol.
1918	Auguste J. Rossi	Achievements in field of titanium steel and other titanium alloys.
1919	F. G. Cottrell	Recovery of helium from natural-gas wells and electrical precipitation of suspended particles.
1920	Charles F. Chandler	Work as educator and expert in field of industrial chemistry, as pioneer in field of sanitary chemistry, and for invention of system of assay weights.
1921	Willis R. Whitney	Achievements as research director of General Electric Company, in development of metallized incandescent filaments of Gem lamps, tungsten lamps, gas-filled lamps, insulating materials, alloys, and new apparatus and electric equipment.
1922	William M. Burton	High-temperature process of cracking petroleum under pressure.
1923	Milton C. Whitaker	Achievements in manufacture of alcohol, ethyl acetate, acetone, other solvents, and the utilization of by-products.
1924	Frederick M. Becket	Processes for extraction of rare metals from ores, manufacture of calcium carbide, and reduction of rare metals and alloys.
1925	Hugh K. Moore	Development of electrolytic processes for chlorine and caustic soda, and recovery and utilization of by-products in pulp and paper industry.
1926	R. B. Moore	Achievements in field of helium and radioactive elements.
1927	John E. Teeple	Achievement in manufacture of acids, alkalies, chlorine, permanganate, special chemicals; design of plants for same, distillation of hardwoods; utilization of pine oil; and chiefly for recovery of potash and borax at Searles Lake, Calif.
1928	Irving Langmuir	Accomplishments in field of low pressures; conduction, convection, and radiation of heat; vapor pressure of metals; new vacuum pumps and vacuum gages; atomic and crystal structure; electronic and ionic currents; high-power vacuum tubes; theories of absorption, evaporation, and passivity; first to apply argon and nitrogen in tungsten lamps; atomic hydrogen flame for welding; and conception of space charge in thermionic tubes.
1929	E. C. Sullivan	Development of special glasses for heat resistance, for transmission of certain light rays, and for other purposes.
1930	Herbert H. Dow	Developments in bromine and electrolytic production of chlorine and alkali; in manufacture of metallic magnesium and its salts; and in introduction of novel processes for phenol, aniline, and other organic chemicals.
1931	Arthur D. Little	Work as a pioneer in the application of research to industry and development of processes for chrome-tanned leather, chlorate of potash, cellulose acetate, smoke filters, newsprint from southern woods, recovery of naval stores from lumbering wastes, and vapor-phase cracking of petroleum.
1932	Charles F. Burgess	Work on electrolytes, electrolytic iron and its alloys; metallurgy of zinc, corrosion of iron and other metals, and development of the dry cell.

Accomplishments of the Medalist

Howard F. Weiss

VISUALIZE a wiry newsboy in his early teens bucking the snowdrifts and icy winds in a small town in northern Wisconsin in order that its citizens might regularly read their daily paper in comfort, and you have the genesis of Charles Frederick Burgess' contact with our everyday world.

The lessons of punctuality, responsibility, and determination, accompanied by a direct appraisal of human and material values which he thus learned on his newspaper route, left their indelible stamp upon him, and served him in later years as no other adolescent teachings could have done.

C. F. Burgess

When he entered the Engineering College at the University of Wisconsin he had a much clearer conception of why he was there and what he wanted than is the lot of most students in their postgraduate years. It is not surprising, therefore, that we find him a leader in his class and a member of Tau Beta Pi. Upon graduation in 1895, at the request of his tutors he remained to become an assistant in electrical engineering. During his instructorship he recognized the growing industrial importance of chemistry and took special courses in this science. When promoted to the rank of assistant professor, he established at Wisconsin a course in applied electrochemistry. This was the first course to be given in this subject in the United States. Later, with the rank of professor he established the course of chemical engineering and was made its director, which position he held until his resignation.

While at the University, Doctor Burgess, in addition to his teaching, did a tremendous amount of research and consulting work, some of which laid the foundation for important industrial operations as we know them today. It was a practice of his to bring the workaday problems of industry into the classroom where he discussed them with his associates and students. One of his former students, now a professor in chemical engineering, told me that this practice did more to stimulate in the boys a genuine interest in their work than he has yet seen developed by any teaching method. In his opinion, one of the most outstanding achievements of Doctor Burgess was his ability to instil real red-blooded enthusiasm in his students toward their work, and this professor asked me to be sure and record this in my recital of Doctor Burgess' achievements.

At the beginning of the present century the bicycle was a sporty and popular form of locomotion. The manufacturers of these machines were put to expensive and tedious means of removing the surplus brazing metal from the bicycle frames, so that this was a very real problem in the industry. One of Doctor Burgess' earliest industrial achievements was the development of an electrochemical method for removing this excess brazing metal. The method was so simple and it worked so beautifully that it soon displaced the old hand filing and grinding practices then in vogue, and became universally adopted as the means of removing brass as well as other metals from iron.

As a companion project Doctor Burgess demonstrated the commercial utility of the electrolytic cleaner. This afterwards was adopted by industry as the standard practice for cleaning metals preparatory to electroplating them.

The next contribution of this struggling young professor in the field of applied electrochemistry caused him, at the time, severe financial loss and disappointment but served him well in the years that followed. He had done a prodigious amount of work in an attempt to convert alternating into direct current. As a result, he perfected a fused salt aluminum electrolytic rectifier that worked beautifully. He filed application for a patent on his idea, and all was going nicely until he ran afoul of a large electrical company in the East. The patent interference established seemed well on the road to a successful conclusion, when a budding patent attorney employed by this electrical company unearthed an obscure Russian periodical which revealed just enough information to prevent the fruition of Doctor Burgess' dream, and a patent was denied him. But he had the satisfaction of having made a good fight and of seeing his ideas put into wide manufacturing usage.

I cannot pass this episode without pausing to record an interesting human incident connected with it. The young attorney, whose arduous labor in searching the world's literature was responsible for defeating Doctor Burgess, was one of his own former students! But here we see the lessons, learned as a newsboy, now surge to the fore. Doctor Burgess at his first opportunity turned around and hired that young man to be his own patent attorney. Practically all of Doctor Burgess' later patents were not only taken out, but have been defended in court when necessary by this attorney.

Perhaps Doctor Burgess' outstanding technical contributions were in the development of a process for making electrolytic iron and the making of alloys from such iron. This was closely associated with his studies in the general field of corrosion. This work was so favorably recognized that he was given a grant of $10,000 by the Carnegie Institution to continue his studies. Over a thousand alloys were made and investigated, the data being published largely in the *Transactions of the American Electrochemical Society* and in *Metallurgical and Chemical Engineering*. These studies furnished the basis for the commercial production of electrolytic iron in the United States and in later years, during the World War, France sent Captain L. Boyer to this country to consult with Doctor Burgess to get his help in establishing a plant in France.

Among the more important results of this work which have since found wide industrial application might be mentioned the following:

(1) The addition of a small amount of copper to iron makes it much more resistant to atmospheric corrosion. Adherence to his conclusions, based on these discoveries in this field, caused much sharp and at times bitter criticism to be levied against him, but Doctor Burgess' position has been substantiated by the test of time.

(2) Electrolytic iron of high purity has exceptional magnetic qualities.

(3) Iron-monel or iron-nickel-copper alloys have exceptional mechanical qualities.

(4) Certain iron alloys have electrical properties which make them suitable for heating elements.

(5) Certain of the iron alloys have magnetic properties which make them suitable for permanent magnets—a piece of work which has proved of such great value in the development of permalloy for telephone transmitters and for other industrial applications.

C. L. Mantell in his book on "Industrial Electrochemistry," recently off the press, writes as follows:

> The first serious attempt to produce electrolytic iron in quantities was in 1904 when the metal was deposited from a mixture of ferrous and ammonium sulfates at a c. d. of 6 to 10 amp. per square foot (0.65 to 1 amp. per sq. dm.) at 30° C. and an average e. m. f. of 1 volt. This method came to be known as the Burgess process, and, with some variations, has been a basis for most commercial manufacture of electrolytic iron in the United States. In the plant of the Western Electric Company the anodes were cast steel, and the bath carried slightly on the alkaline side so that a considerable amount of oxides would be deposited in the cathode to make the latter brittle and easily ground up in connection with the manufacture of electrical "loading coils." It was not necessary to make a pure grade of iron. A further modification of the Burgess process was used by the Westinghouse Electric and Manufacturing Company in which a pure grade of iron was produced for use in the manufacture of alloys for electromagnetic machinery and instruments.

In 1908 when Doctor Burgess was elected president of the American Electrochemical Society, he disclosed in his presidential address the work he had done in boiler corrosion and showed its electrochemical nature.

His studies in the corrosion of iron in concrete were considered such a valuable contribution to the art that the Western Society of Engineers in 1911 awarded him the Octave Chanute Medal.

About 1910 there was much heated discussion between trolley companies and various gas, water, and telephone companies on the causes of and proposed cures for corrosion of gas and water mains. This was a serious and acute problem at that time. Doctor Burgess worked very actively in this field of stray-current electrolysis and made a large number of surveys in many cities in the United States. His explanation of the causes of and the solution for the problems thus encountered subjected him to much criticism and attack, but he has lived to see his early recommendations justified and his proposed solutions adopted.

His work in stray-current electrolysis was very much in the public eye, so it is not strange that he should have been drafted to grapple with another problem in which the public interest was also at stake—namely, the calorific value of gas. The Wisconsin Railroad Commission put Doctor Burgess in charge of its light and heat departments, and after almost insurmountable difficulties he succeeded in having gas put on a heat-value basis in Wisconsin. This was the first state to adopt this standard, and so far-reaching were the results obtained that the Wisconsin standards have now become universally adopted.

While associated with Jasper Whiting, Doctor Burgess entered the field of paper-making and conducted experiments at Rumford, Maine, with the mercury–caustic soda cell. He removed the oxide film by electrochemical means and secured a complete oxidation of the sodium amalgam, thereby greatly improving the workability of the process.

The art of galvanizing also commanded Doctor Burgess' attention, and his studies improved both hot-galvanizing and electrogalvanizing practice. In the Sherardizing process he showed that it was possible to replace the commonly used zinc dust with the zinc-iron alloy, $FeZn_{10}$, which he made from galvanizers' dross. He showed that the zinc-iron alloys formed in hot-coating methods are galvanically protective to iron, thereby correcting earlier published data and conceptions.

Doctor Burgess also worked on the electric-furnace smelting of zinc. He devised methods of roasting zinc ores and then concentrating magnetically. These studies were later followed up by Fulton at the Missouri School of Mines.

Doctor Burgess devised a method for separating articles in the electric furnace to prevent their fritting together in the intense heat of the reaction zone. This method is used extensively in electric-furnace practice.

His success in applying chemistry and engineering to the problems of industry attracted the attention of business executives to such an extent that Doctor Burgess decided to establish an industrial research laboratory of his own. This he did in 1910 under the name of Northern Chemical Engineering Laboratories. As this institution grew, he reorganized it later under the name of C. F. Burgess Laboratories, and still later the C. F. Burgess Laboratories, Inc., under which name it is now in operation.

One of the major projects of his laboratory was the study of the dry battery, and on this product Doctor Burgess and his associates have done a prodigious amount of work, resulting in over sixty patents and in the material improvement of this useful device.

He found the triple duties of teacher, consulting engineer, and manager of his own company too exacting on his time and strength, so in 1913 Doctor Burgess resigned from the University of Wisconsin to devote his entire time to his own growing business. Severed from his academic atmosphere, he now found himself a full-fledged business man. Many were the heartaches this change brought to him. His struggle with labor, bankers, and pay rolls make a most fascinating story but fall outside the province of this paper.

Early in his business career he decided to put to his own use the technical knowledge which he had been so successfully supplying to others through his consulting activities. Consequently, he organized in 1917 a company of his own to manufacture and sell dry batteries. This was called the Burgess Battery Company, under which name it is now known throughout the world. The problems of finance, personnel, manufacture, sales, and advertising demanded so much of his attention that they made sharp inroads on Doctor Burgess' time for exercising his scientific talents. Nevertheless, he found time to work in his laboratory, and many of the technical contributions of his companies are the result of his personal genius and skill.

For example, he applied the principle of overvoltage to dry-cell construction when the price of zinc mounted rapidly during the World War and threatened his infant company. He substituted terne and tin plate for zinc bottoms in dry cells at a very considerable saving in cost.

He devised a unique and efficient method and apparatus for sterilizing liquids with nascent chlorine generated electrochemically. This method was successfully used in certain hospitals to treat badly infected wounds and gangrene.

He devised, on short notice, methods for producing and purifying silicon and titanium tetrachlorides, which methods were used for producing large quantities of these chemicals during the war.

He materially improved the shelf life and capacity of dry cells.

He developed methods for chemically treating and purifying low-grade and impure manganese dioxide ores to make them suitable for use in dry cells. When the World War shut off the supply of Russian manganese dioxide ores and the German artificial manganese dioxides largely used in dry cells, he established a plant which was successful in recovering and purifying the manganese dioxide contained in worn-out dry cells for re-use in making new cells. This plant was based on several years of research prior to the war and exemplifies Doctor Burgess' foresight in preparing for any exigencies which may arise in the future.

He developed the use of impalpable graphite in dry cells. In fact, this pioneer work in studying the chemical and electrochemical relations in dry-battery cells resulted in such an accumulation of data that the United States Government sent its responsible engineers and chemists to his plants to acquire this knowledge when it became necessary to construct new types of cells and batteries during the World War.

The Burgess Battery Company has grown until it now has plants at Madison, Wis., Freeport, Ill., Niagara Falls and Winnipeg, Canada, and at Earl Shilton, England. Its products have been an essential part of the equipment of many notable explorations. Burgess batteries have been flown over both poles and around the world and are now known in practically every civilized country.

While the manufacturing and marketing of dry batteries have constituted the major part of Doctor Burgess' activities of late, his activities have by no means been confined to them.

In 1928 he became associated with the late Samuel W. Parr and reorganized the Standard Calorimeter Company into the Burgess-Parr Company. This company manufactures at Moline, Ill., a line of scientific instruments, some of which, such as the Parr calorimeter, are now standard laboratory equipment.

Through his encouragement and direction, the Burgess Laboratories developed from the waste of sawmills two heat-insulating products now widely sold throughout the United States by the Wood Conversion Company of Cloquet, Minn., under the trade names of Balsam Wool and Nu-Wood.

After years of painstaking research, the Burgess Laboratories developed a stereotype dry mat, now sold throughout the United States and Canada by the Burgess Cellulose Company, of which Doctor Burgess is chairman of the board.

A recent triumph of his laboratories was the successful commercial fermentation, on the largest scale heretofore attempted, of molasses into butyl alcohol.

At present Doctor Burgess is devoting much of his attention to the comparatively new field of acoustics. Under his direction a new type of acoustic treatment was developed; it is known to the trade as Sanacoustic Tile and is now marketed throughout the world by the Johns-Manville Corporation.

He has recently patented a highly effective means of demonstrating the absorption of sound waves through perforated metal.

Another important development of the Burgess Laboratories, employing acoustic principles heretofore overlooked, has been the silencing of the exhaust gases of internal-combustion engines. Burgess mufflers are now in use by thirteen automobile companies in the United States and England. While giving excellent silencing, they practically eliminate back pressure, thereby adding more power to the engine.

In recognition of his activities as an inspiring teacher, for his contributions in the fields of pure and applied science, and for his accomplishments in the business world, the University of Wisconsin conferred on Doctor Burgess in 1928 the honorary degree of doctor of science.

To his associates and to his hundreds of employees he is their respected and beloved leader, always more willing to give than to take.

Research "For Pleasure or for Gold"

Charles F. Burgess, *C. F. Burgess Laboratories, Inc., New York, N. Y.*

TO THE Perkin Medal Committee and to the societies you represent I offer my humble and sincere thanks for the honor conferred upon me. No words can I find which enable me to express the depth of my appreciation of this evidence of regard from men whose opinion I value.

I realize fully that the favorable light by which you have viewed my work is a reflection of that which had been shed by the brilliant and able men and women with whom I have had the good fortune to be associated, and it is with those who have worked with me that I wish to share the honor of this award.

This invitation to address you I take as a courteous challenge to say something which may be useful or instructive regarding the work I have been doing. For thirty-seven years I have been engaged in various forms of scientific research; in that designated as pure science where the results are given to the public; in that sponsored by the government where the results are forced upon the public; and in industrial research where the results are sold to the public. Out of this experience I am able to say that the greatest pleasure to be derived from research is that which comes to the worker when freed from all thoughts of cost or of the economic value of the results.

Studies on Electrolytic Iron

Of my numerous studies it was the one relating to electrolytic iron which brought no pecuniary reward but the greatest personal satisfaction. The idea which started this investigation was a statement published in a metallurgical journal that pure iron was needed greatly for fundamental research on iron and steel, and that attempts to produce electrolytic iron had yielded only one sample weighing a few grams.

Accepting this as a challenge, and with the coöperation of a graduate student, I undertook to excel the record. A refining process was developed, and, after continuous operation of a small electrolytic tank for 40 days and 40 nights, a plate of iron weighing 20 pounds was brought to view. If the alchemist, vainly seeking to transmute base metal into gold, had found that he could pour a stream of the precious substance from his crucible, he would have had no greater thrill than we on taking from our tank that white, shiny, warty chunk of iron.

In our greed we wished to make more, not only for ourselves but enough to share with other investigators. But our funds were exhausted and we could not go on. Then a bright ray of hope came to us in the public announcement that the Carnegie Institution of Washington was about to make available to worthy investigators various sums of money for carrying on meritorious research projects.

We felt that we were worthy and that our plan was meritorious, but we had to prove it; and so, before making our formal petition, we sought and obtained the approval of various prominent scientists, among them being H. M. Howe and Sir Robert Hadfield. Encouraged by such endorsement, our request was submitted, and after a period of breathless waiting the great news came from Washington that favorable action had been taken. Ten thousand dollars was to be made available, to be spread over a period of five years. A restriction was imposed. We were prohibited from applying for patents or otherwise commercializing the results of the work.

With such an opportunity open before us, other assistants were employed, several tons of electrolytic iron produced, over a thousand alloys made, tests conducted, and the results published.

The joys derived from this work were shared by a group of able and enthusiastic young men who have since earned honorable positions in the scientific and technical world. The group included Oliver P. Watts, Carl Hambuechen, James Aston, John Thickens, Otto L. Kowalke, and A. Hoyt Taylor.

SERVICES IN LIGHT AND HEAT LEGISLATION

About this same time I had an opportunity for public service under the direction of Governor Robert M. LaFollette, that great champion of the masses, who believed that the benefits of science should be made available to the common people. He had observed that the oil lamps in the country homes and the oil lanterns carried by the farmers gave lights of varying degrees of brilliancy, mostly low. He decided that oil inspectors should be appointed; they were to be equipped with photometric instruments and instructed to see that all kerosene sold in Wisconsin should conform to suitable standards. Legislation was passed to bring this about. A committee of scientists and engineers, three in number of which I was one, was appointed to define the candle-power standards for kerosene and design the equipment to be carried by the inspectors.

After collecting a large variety of burners and many samples of kerosene sold by dealers throughout the state, we made careful photometric tests. To our consternation these revealed the fact that all the grades of kerosene gave identical candle-power values; the differences in illumination from the lamps and lanterns were found to be dependent upon the care and frequency with which the wicks were trimmed and the chimneys cleaned. The committee was then discharged and the people were left to their own devices.

But a better opportunity came later when it was decided to regulate the gas and electric service furnished by the public utility corporations. To me was assigned the duty of formulating rules and standards, and thus by legislative action rather than by qualification I acquired the title "Expert on Light and Heat." A part of the work then undertaken involved an exhaustive study of gas calorimetry. Through an investigation of the technology of gas manufacture, with the coöperation of gas experts called into conference, standards of calorific value were determined and prescribed by law. Because of this, I believe that to Wisconsin should go the credit for being the first state in this country to enforce by legislation the abandonment of the candle power and the adoption of the heat unit as a measure of gas value.

ORGANIZATION OF COMPANY TO MAKE RESEARCH PAY

But the joys of research in pure science and in public service were not unmixed with sundry trials. During one of the recurring reform waves, it was stated on the floor of the Wisconsin Assembly that all was not well at the State University; that the professors were neglecting their educational duties; and that one of the worst offenders was Burgess who was the recipient of large sums from the vested interests, notably ten thousand dollars from Carnegie.

A committee was appointed to investigate these disgraceful affairs, and I appeared before this committee and the governor. I explained that the money received from the Carnegie Institution was used for the promotion of research at the university for which the university received credit; also that my university salary and other sources of income afforded but modest living comforts. No drastic action was taken so far as I knew.

Then in 1910 came the launching of a most hazardous venture. With three of my younger associates numerous meetings were held, at which we discussed the prevailing condition of poverty among teachers, the limitation on research imposed by university conditions, and the economic value of scientific discovery. We reasoned that if research had value, the results should be salable, and that, if so, the money received could be employed in financing more extensive development work.

With our imagination fired by such possibilities, we proceeded with our plans to organize a company. The greatest obstacle standing in the way was the lack of necessary capital, but by pooling our joint resources, which consisted in a combined borrowing capacity of nine thousand dollars, a company was organized and incorporated. We proposed to undertake the solution of problems in the field of chemical engineering and then to prove that industrial research could build its own endowment.

It was not with universal approval that my academic friends learned of my plans. Quite the contrary. I was accused by former colleagues of abandoning the higher standards of scientific ethics and becoming "a dollar chaser." But these criticisms were trivial compared with the trials and reverses we soon encountered as the experiment got under way, for with no precedents or business experience to guide us we had our difficulties and disappointments. But also we had some success. Now after twenty-two years this company is still in existence, and long ago the original indebtedness of nine thousand dollars was discharged.

There was no dearth of ideas nor of problems upon which to work. Necessity compelled us to consider the results of research as a commodity for which buyers must be found. No eagerly receptive market awaited us. The value of research as an adjunct to industry was well recognized, since many of the larger industries had research departments, but the cost of research, even at the moderate rates at which we tried to sell it, was an obstacle to securing suitable clients.

Then the novel idea was presented: "If industry does not want to employ us as an adjunct, why not reverse the plan and make industry an adjunct to research?" It proved to be a good suggestion. We engaged in the manufacture and sale of products embodying research results; organized several companies in which we retained interests and representation; and thus, when waves of economy or depression came, were in an authoritative position in presenting the case for research to the budget committee.

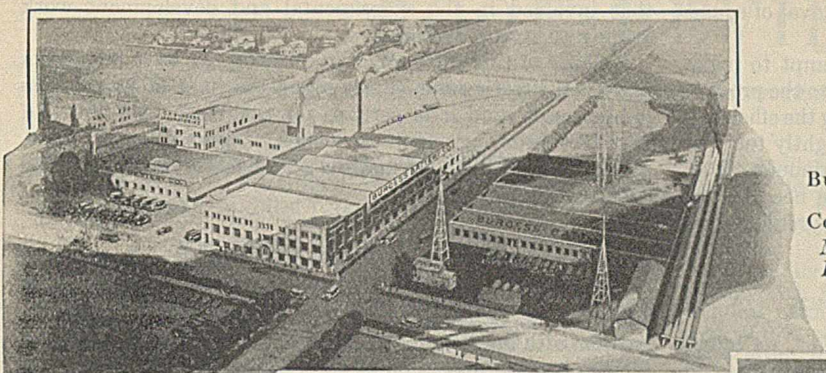
How many people in our organization are engaged upon research? This is a question I cannot answer. It may be ten, or a thousand, or an intermediate figure according to the definition of research. This term has come into indiscriminate use to designate all effort directed toward improvement. A simple inquiry into a factory operation, or taxation, or distribution of sales, or buying power of the public is often called "research."

The term "research project," as employed by us, means a course of investigation of an idea which promises to be of commercial value, involving study and supervision by men trained in science; testing and proving on successively larger scales; and at last, from a pilot plant or semi-commercial operation, the drawing of final conclusions. A completed project may then be ready for commercial demonstration. One hundred and fifty such projects have entered on our records since 1910. Thirty of these have emerged as being worthy of commercial development.

Of ideas presented there is always a superabundance. Many of them come from the outside, but a larger number come through evolution during an investigation.

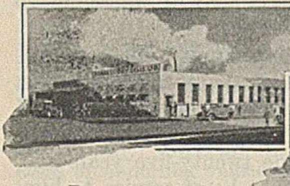
When a man with the prospectus of a new device or product

THE BURGESS ORGANIZATIONS



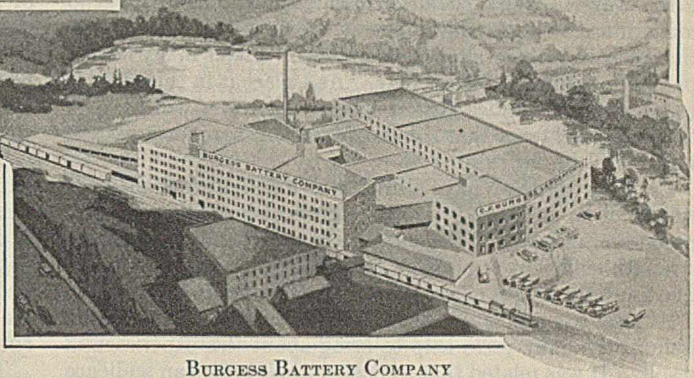
Burgess Battery Company
Madison, Wisconsin

Burgess-Parr Company
Moline, Illinois



Burgess Dry Cells, Ltd.
Winnipeg, Manitoba

Burgess Battery Co.
Niagara Falls, Ontario



Burgess Battery Company
Freeport, Illinois

or process presents himself, I have a mixed feeling of interest and of resistance, for I have to tell him that to put it through the laboratory course may involve a cost of a thousand dollars, perhaps a hundred thousand. Our average for all projects has been seven thousand dollars. I must tell him that, no matter how practical the idea he presents may seem to him or to us, there is but one chance in five that it will pass successfully through the laboratory stages; furthermore, that the investigation, if it survives the full course, may take anywhere from one to fifteen years, with the probability of seven as an average.

It is with these figures in mind that we have come recently to appraise any new proposal for a research project.

Evolution of Research on Cotton

From the list of our investigations the impression might well be conveyed that the subjects were chosen in an illogical hit-or-miss fashion. This is because a laboratory pursuit leads into devious pathways. As an example, during the Great War cotton became scarce and almost unobtainable, even for such important uses as surgical dressing on the battle front. It was suggested at a laboratory conference that a good substitute could be made from wood pulp. This was entered as a project, an emergency measure. Rapid progress was made. In the process as evolved, a white bleached pulp was first converted by special disintegrating machines into what resembled a snow storm of cellulose fibers. This came into contact with a cloud or mist of adhesive, the combined material settling quietly on a moving screen, then passing through a drier, and emerging as a thick sheet of porous structure, well adapted to the specification of a surgical absorbent bandage.

Before regular production was started, the war stopped and the material became unnecessary. Seeking a method of salvaging this development, we studied the properties of the material and its adaptability to other uses. An outstanding characteristic was its heat-insulating property; another its ability to absorb sound. To develop a commercial use as a building material, it was necessary greatly to reduce the cost, which was done by eliminating the bleaching operation and by using a cheaper grade of material—pulp-mill screenings. Thus evolved the commercial product known as Balsam Wool.

A side issue now came into the program. It was noted that, by disintegrating wood and by grinding it for suitable time in the presence of water, and then pressing and drying, boards of any desired degree of density and strength could be made. Thus originated the expression "boards 8 feet wide and 16 feet long from trees 2 inches in diameter."

The outcome of these two projects was the erection of a mill at Cloquet, Minn., where the entire wood waste of a large lumber mill is now being converted into commercial products of value greater than is the lumber of which the waste is a by-product—certainly a long step taken by the Weyerhauser Lumber Company in the interests of forest conservation.

The adaptation of the porous cellulose material to sound-deadening purposes introduced us to new problems requiring solution. It became desirable to develop a protective covering which would give rigidity and permanency to the wall surfaces on which the absorbent was applied.

A discovery was then made (simple enough to be important) that when sound waves strike a metal plate perforated with small holes and backed with sound-absorbent material, the metallic surface does not reflect the sound. In fact, evidence points to a greater effectiveness of a sound-absorbent material if faced by a perforated metal plate than without it. The metal screen thus affords a surface which may be painted and decorated, as well as giving strength and fire-resistant qualities. This type of structure is now extensively used in architectural acoustic treatment.

In an attempt to apply the perforated-plate idea to the quieting of the exhaust of gas engines, perforated sheet iron was formed into a tube and surrounded by a heat-resistant absorbent material, such as steel wool held in place by an outer iron cylinder. By conducting the pulsating exhaust gases through the inner pipe, an almost complete removal of sound was produced, and with no back pressure.

Thus by a series of steps, the original attempt to make bandages for wounded soldiers evolved finally into the production of mufflers for absorbing noise and increasing the efficiency of automobile engines. But those steps, thus lightly touched upon, covered a period of fourteen years of continuous effort. One factor that made for slow progress was the necessity of developing instruments and methods for measurement and analysis of sound waves.

Development of New Type of Brick

Thus, engaged in a study of building materials, we found many ways in which chemical research might be directed to modern architectural development. I shall give one illustration by performing a simple experiment. I have in my hand a piece of brick made from a clay. As I place it in this glass of water, you will notice that it floats. And you will have to take my word for it that if I should leave it here for a year, it would still be floating.

In other words we have a brick which is light (one-fifth the weight of an ordinary brick), of high heat-insulating quality, porous yet resistant to the entrance of water, and of a crushing strength sufficient to support its weight if built into a tower five times the height of the Empire State Building.

At least to some extent did the appearance of a certain news item in the daily press help to bring about this experimental result. It was related that a speaker arose before an audience in England to discuss the prevailing high cost of building. He took out his watch, held it before him, and looked at it intently without moving a muscle. Curiosity of the audience at this strange behavior turned to wonder and then to impatience when the speaker finally said: "That, ladies and gentlemen, is the length of time it takes a brick layer to lay one brick—66 seconds."

I showed this dispatch to Howard F. Weiss, who was then studying the possibility of improvement in brick manufacture. He made a mental calculation and said, "Under the prevailing rates, it costs four times as much for the labor of laying a brick into place as it does to manufacture it. Why not make a brick so that with a given physical effort two bricks can be laid at one time and with the same motions that are required to lay one?"

This in fact now appears possible; it has not been accomplished, as the technical practice has not been perfected. Although the process is still in the development stage, the outcome looks promising.

Even when a process or product has been approved in the laboratory, it is not an accomplished success, for it must then share in the hazards which all new commercial ventures experience. It must answer the question, "Does the public want it?" Our experience is that telling the people about it is a far more expensive operation than is the cost of research leading to the development of a new product or process. It is a common experience to find that the cost of impressing upon the public even the name of a new product may be ten times that involved in the experimental and development work leading to its production.

Because of this commercial uncertainty we have adopted a policy of directing our efforts along the lines of prospective public needs, and it is perhaps for this reason we now find ourselves working upon acoustics, suppression of noise, purification of air, and materials and methods for building construction.

New Problems in Research

As to the outcome of our experiment to make research pay its own way, of making industry an adjunct to or at least a partner with industrial research, I might point to our increase in membership, our buildings and equipment and interests in manufacture as showing reasonable success. But I must qualify this by saying that our research ability is no magic power by which we can free ourselves from the evils which have fallen upon all business and all people. I wish, therefore, to withhold judgment.

That the scientist realizes the opportunity and responsibility which now confronts him is illustrated by a conversation I had not long ago in London with Sir Robert Hadfield. I had called upon him to pay my respects, to thank him for the notable service he had rendered me twenty-five years ago, and to express the wish that I might be of service to him. He said, "There is one thing I want. Tell me how I can give employment to one hundred men?" And here I failed.

There is a continually changing economic background against which research must be judged. Only a few years ago the effort to relieve the drudgery of human labor by automatic machines was most praiseworthy, and now we are looking for something for people to do. The farmer who wrote to the Agricultural Experiment Station had a real complaint when he said, "You once told me a secret of how to make two blades of grass grow where but one grew before. Then I found it was no secret as all my neighbors knew about it, and so we are now producing more grass than we know what to do with. Now I learn that you are trying to find how we can make one blade grow where two grew before. I am sadly perplexed about this research business."

The business executive is now being subjected to criticism for his curtailment of research appropriations and his lack of recognition of the value of sustained research; and the scientist is likewise blamed for slowness, impracticability, and failure to solve the problems of peace as he did the problems of war.

The scientist has a great opportunity if he will bring himself to share in the affairs of business, and the business man could forget his troubles if he would but experience some of the joys which come through research. In a partnership of the two lies opportunity for betterment.

And now with this Perkin Medal as an inspiration I return to the work of producing batteries, quieting noise, making bricks, and developing ideas, in the knowledge that from it I shall derive pleasure, possibly produce profit, and I hope that in it will be a measure of public service.

Income from Medical Practice. A study of 6328 random reports of physicians from all parts of the United States indicates that the median gross incomes for the entire group reporting lie in the range \$6500 to \$7499. The largest annual gross incomes are being made by physicians who have had ten or more years of preparation. The low gross incomes fall among those who have had three years or less of preparation. The peak of gross income seems to be reached in the period of fifteen to nineteen years in practice. The gross annual income for the period of five to nine years in practice and the long period of thirty-five to forty-nine years in practice appear to be closely parallel. Although the high average annual incomes for the entire group appear to be reached in the metropolitan areas of 1,000,000 and more population, the low gross averages fall in communities of 2500 and less population. The largest number of salaried physicians have had seven years or more of preparation. In the 6328 reports studied, the percentage of physicians who derive all or most of their income from salary is largest in the population groups of 10,000 to 25,000 and 500,000 to 1,000,000.

BOOK REVIEWS

RECENT ADVANCES IN ORGANIC CHEMISTRY. *By Alfred W. Stewart.* 6th edition, 2 volumes, 861 pages. Longmans, Green and Co., New York, 1931. Price, $3.50.

The present edition of this standard work represents a slight expansion over the first two-volume edition which appeared in 1927 (fifth edition). Some 150 new articles from the recent literature have been included. Many new topics, such as Sugden's parachor and Ruzicka's work on muscone and related large rings are discussed at length. The order of chapters is as follows: main currents in organic chemistry; sundry modern reagents; addition reactions; polymethylenes and large carbon rings; aliphatic diazenes; the ketenes; the polyketides; monocyclic, dicyclic, and olefinic terpenes; pyrrole; pyridine; tropine; quinoline and isoquinoline alkaloids; the purines; the polypeptides; trivalent carbon; unsaturation; orienting influences in the benzene system; organic chemistry in the twentieth century; some carbohydrate constitutions; the sesquiterpenes; the di- and triterpenes; rubber; recent work on the alkaloids; the anthocyanins; the chlorophyll problem; the depsides; some theories of natural syntheses; isomerism in ring compounds; the diphenyl problem; new organo-alkali compounds; other cases of abnormal valency; structural formulas and their failings; some applications of electronics to organic chemistry; some unsolved problems.

An examination of this list of topics will indicate the function of the work—to survey for the busy organic chemist developments in the leading fields of research which would otherwise be available only through a painful search of the literature.

The reviewer is disturbed by only one fear—that this most useful work may continue to expand until it becomes another Beilstein. He would express the hope that the next edition be limited to one volume of modest dimensions, and that it contain more of the author's own impressions of the way organic chemistry is or should be going, such as the passage from the present edition: "in the near future the study of quite simple reactions will offer many points of interest......more interesting and useful work could be carried out by an examination of even such obvious problems as the hydration and dehydration of simple organic compounds."

Frank C. Whitmore

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CHEMICAL ANALYSIS OF IRON AND STEEL. *By G. E. F. Lundell, James Irvin Hoffman, and H. A. Bright.* 641 pages. John Wiley and Sons, Inc., New York, N. Y., 1931. Price, $7.00.

This book is unique in that it has a threesome authorship by prominent analytical stars of the United States Bureau of Standards. Throughout, it reflects their views and technic. The methods are mainly well-known standard ones; also numerous private communications are given from experienced chemists who have been in this work with large manufacturing concerns for years. A notable instance is Chapter XL on ferro-zirconium, silicon-zirconium, zirconium ferro-silicon. The authors state, "The methods are based almost entirely on a private communication from Thos. R. Cunningham, chief chemist, Electro Metallurgical Co."

The plan of the work is in three groups: the ordinary five elements; then the common alloying ones—copper, nickel, chromium, vanadium, molybdenum, tungsten, and cobalt; and third, aluminum, titanium, zirconium, tantalum, uranium, the rare earths, arsenic, tin, zinc, etc., as applied not only to steel but to all ferro-alloys and related ores. Then follow chapters on limestone; high refractories, such as bauxite; slags; coal and coke; molding sands. Fluorspar has 10 pages. Where possible after reviewing in a critical way methods in general, an umpire method is recommended in detail and also a routine one. There are 28 pages on apparatus and reagents; 16 on qualitative tests and separations of iron, including 2 pages on spark tests and 2 on spectroscope; 42 on common operations; and 35 on special operations and volumetric analysis. There is an interesting chapter on accuracy of determinations and standard samples. Under qualitative tests is found the tin content of the cast-iron, Bessemer steels, the B. O. H., A. O. H., and the alloy-steel-standards steels. Further, under Apparatus, on page 6, is a table giving the complete chemical contents of eight standard chemical glasswares.

The chapter on zinc is disappointing, as it is mainly devoted to setting forth the well-known fact that there is no good and practical method for separating small amounts of zinc of the order of 0.02 per cent from iron. One is a little surprised to find space given to the direct carbon combustion by sulfuric and chromic acids, as this procedure was shelved a quarter of a century ago. It should be marked historical. Chapter XXX contains 31 pages describing the earlier and recent work on Methods for the Determination of Oxygen, Oxide Inclusions, Hydrogen and Nitrogen, including those of Herty and Fitterer.

No analytical chemist practicing in this field should be without this treatise but should swiftly sequester seven simoleons, securing it at once regardless of the present "repression." The printing is good. There are 63 figures illustrating the text.

Charles Morris Johnson

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BENZOL (BENZENE) POISONING. *By Carey P. McCord.* 78 pages, mimeographed. 1931.

The monograph describes the pathological effects of gassing rabbits with commercial benzene and a benzene of considerable purity; also with acetonitrile, thiophene, amylene, methyl disulfide, and carbon disulfide in small amounts. The conclusion reached by the author is that the medical symptoms of "benzol" poisoning are caused by C_6H_6 and not by the impurities in the commercial product.

It is unfortunate that physicians describe in great detail the medical part of their experiments and omit important details pertaining to other phases of their problem. A "modified" Yant and Frey method of gassing the animals was used, but no description of this modification is given. Despite the large proportion of space devoted to the literature of the subject and general comments (53 pages), the author says: "Space limitations prevent extensive presentation of details relative to animals and their care, specifications for gassing chambers, dripping apparatus, determination of concentrations." The author has apparently overlooked the fact that accurate determinations of vapor concentration breathed by the animals, and means used to prevent appreciable variations, are of utmost importance in animal experiments on toxic vapors.

A chapter entitled "Practical Protection against Benzene Poisoning" contains nothing that is new and much that is obsolete. It is an example of a physician attempting to pass judgment on an engineering problem.

The bibliography is very extensive. P. W. Gumaer

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PRINCIPLES AND PRACTICE OF ELECTROCHEMISTRY. *By C. J. Brockman.* 348 pages. D. Van Nostrand Co., Inc., New York, 1931. Price, $4.00.

This book takes as its subject matter substantially the entire field of electrochemistry, discussing first: general principles; reactions at the electrodes; the electrometallurgy of solutions and the common metals; and the production of caustic soda, chlorine, hypochlorite, chlorate, hydrogen, and oxygen. It then discusses the electrochemistry of gases and the chemical production of electricity or primary and secondary cells; and the electrolysis of fused electrolytes and the electrothermal processes, such as the manufacture of silicon carbide. Electric furnaces are discussed generally and with respect to their application in the manufacture of phosphoric acid and in the making of iron, steel, and steel alloys.

In the preface the author says, "An effort has been made to present electrochemistry in not too technical a manner so that it will interest the chemist, the plant manager, the manufacturer, and the fringe of business men who are not necessarily adepts with electrochemical manipulations; yet it is hoped that the scientific value of the work will not be lost to the *virtuosi* of electrochemistry. A happy medium is sought, making the contents available to all who are interested in chemistry, either as manufacturers or as research investigators, and to those who have an academic interest in chemistry." The scope of the subject matter attempted in a work of this size necessarily means that each subject must be treated briefly. The reviewer feels that this and the effort of the author to present the material in "not too technical a manner" have led to a book that may be characterized as a descriptive rather than a critical treatment. It might have been wiser to have devoted more space to those processes which are of major commercial importance and to have omitted those of lesser importance. The book contains some errors and would also benefit from better proof reading.

E. M. Baker

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DIE CHEMISCH-TECHNISCHE FACH- UND PATENTLITERATUR ÜBER PRESSHEFE UND GÄRUNGSALKAHOLE, 1914–1930.

By F. Wagner. 249 pages. F. Wagner, Uferstrausse 195, Aussig, Czechoslovakia, 1931. Price, 160 Kč.

The voluminous additions to the technical literature each year are making it increasingly difficult for the average professional man to keep informed in even his own special lines. Searches of the technical and patent literature to learn the status of a particular process are time-consuming and expensive. It is for such reasons that books like this are to be particularly commended, giving as they do, rapid and yet complete cross sections of certain industries.

The volume covers the principal technical and patent literature for the years 1914 to 1930, and deals chiefly with such subjects as production and use of ethyl alcohol in motor spirits; production of ethyl alcohol and acetone, butyl alcohol and acetone, and yeast by bacterial means; continuous fermentation processes; the production of and various factors dealing with yeast, etc.

The references consist of brief abstracts taken almost exclusively from *Chemisches Zentralblatt* and are arranged according to subject matter. In addition, very complete subject, patent, and author indexes assist the reader in quickly locating a particular reference.

The principal defect is the lack of completeness. Only a portion of the technical literature of the period has been selected and in some cases important references have been omitted. The patents abstracted are limited to those of sixteen countries. In a number of instances the patents of a particular country have been included for only a portion of the period covered, and in other cases patents have been omitted which apparently should have been included under topics considered by the author. Both of these factors detract somewhat from the value of the book, particularly to the patent attorney to whom completeness is usually essential. The inclusion of references relating to equipment used in the fermentation industries would have added materially to that value. All of these minor defects will doubtless be remedied, however, by the author in forthcoming editions in which it is planned to keep the book up to date. The reviewer regards this as a valuable addition to the library of anyone interested in any way in the fermentation industries.

F. M. Crawford

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WARMEWIRTSCHAFT IN DER ZEMENTINDUSTRIE. BAND X. WÄRMELEHRE UND WÄRMEWIRTSCHAFT IN EINZELDARSTELLUNGEN.

By Hans Bussmeyer. 96 pages. Theodor Steinkopff, Dresden and Leipzig, 1931. Price, 6 marks.

Industry feels today, possibly more than ever before, the necessity of economy which may aptly be directly towards economy in the energy requirements of plants. In order to meet these demands in the light of the most recent developments, a series of books was planned in which the theory of heat and heat economy was applied to individual industries, and this volume, "Heat Economy in the Cement Industry," is number 10 of the series.

This represents one of the first attempts to treat the subject in a comprehensive manner, and therefore should be a valuable guide for further practical developments. If the volume falls short of adequate treatment of its subject, it is to be blamed on the shortsightedness of the industry itself, rather than on the efforts of the author. For he complains with justification in his foreword that the literature on heat technology in the cement industry is scarce, owing to the policy of the industry in withholding data which have been assembled, or to the fact that the data available are often inexact and incomplete because of the incompetence of the engineers who are employed to assemble such data. Not until these policies are altered can the subject be treated in the comprehensive manner which would be desirable.

The purpose of the work is not to furnish a collection of practical measurements, but rather to give an understanding of how heat economy may be effected by the development of typical problems. The author has stressed sufficiently the theoretical aspects in order that one may fully grasp the significance of the steps in his examples.

Following a short introductory discussion of cement itself, the theoretical heat requirements during clinkering are calculated. The composition of the kiln gases and the evaluation of the related heat balances are treated before entering into a discussion of the various types of furnaces used for the burning of cement. In addition to the rotary kiln, the automatic-shaft kiln is discussed in detail. The drying of the raw materials and of the coal is considered from the standpoint of the thermal requirements in those processes. Then follows a study of power consumption in the plant and the evaluation of such data. Finally, the recovery of heat from the waste gases for the production of steam and power is discussed.

Throughout, the author has referred to German sources frequently, although American data have also been included.

The publishers are to be commended for their workmanship in printing and assembling the book. L. T. Brownmiller

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DIE POLYSACCHARIDE.

By Hans Pringsheim. 3rd edition, completely revised. Julius Springer, Berlin. Price, bound, 26.80 marks.

Probably no branch of chemistry has undergone such fundamental changes in the last six or seven years as that of the polysaccharides, and the reason is not far to seek. Such subjects as the nature of plant synthesis; animal metabolism; industrial manufacture of sugar; starch; pulp; paper; textiles; lacquers, etc., have assumed an ever-increasing importance. As a result of this the fundamental reactions on which these changes are based have been subjected to a much more intensive study, and our ideas regarding the structure of the polysaccharides have completely changed.

The valuable earlier work and views of Irvine in the field of carbohydrate chemistry have undergone a drastic revision, principally under the stimulus of researches carried out by Haworth, Levene, Hudson, Helferich, and Freudenberg, while our knowledge of the chemistry of the polysaccharides has been largely increased through the labors of Bergmann, Hess, Herzog, Karrer, Pringsheim, Meyer and Mark, Zemplen, and others.

The present volume, which thus appears at an opportune moment, represents a completely revised and reëdited edition. The subject matter is arranged under two main headings—(*a*) simple polysaccharides, (*b*) complex polysaccharides.

The former class is divided into four main types—namely, the trehalose, maltose, amylose, and anhydride groups; the latter includes the natural products, cellulose, starch, etc.

Pages 1–64 contain a description of the structure and properties of trehalose, sucrose, maltose, cellobiose, gentianose, turanose, etc., and include short references to the synthesis of such products by chemical action and by ferments. A more extended review of the latter subject would have been timely and of much interest to students and workers in this field.

In the description of Pictet and Vogel's assumed synthesis of cane sugar, the author is careful to point out that the results have not, up to the present, proved reproducible, and, in the reviewer's opinion, until this is the case, the validity of the work would seem to remain an open question.

In part (*b*) a good up-to-date general review is given of recent work dealing with the structure and properties of cellulose, amyloses, dextrines, starch, inulin, and hemicelluloses.

The author's assumption (page 68) of the structure of alkali cellulose as $(C_6H_{10}O_5)_2 \cdot NaOH$ has been disproved by later work [*J. Am. Chem. Soc.*, 52, 3257 (1930)].

In the section on cellulose ethers and esters (pages 72 et seq.) the reader is introduced to the valuable work of Hess on crystalline cellulose trimethyl ether and acetate. The properties of these substances in solution still offer one of the most interesting and baffling problems to the student of physical and colloid chemistry.

With reference to the action of hydrobromic acid on cellulose, much higher yields of bromomethyl furfural than those quoted have since been obtained [*J. Am. Chem. Soc.*, 45, 176 (1923)].

A description is given of the relation of cellulose to lignin and of present views regarding the structure of the latter substance, none of which, it would seem, considering the uncertainty still existing in this field, should be taken too seriously. Chapter V, dealing with the structure and properties of starch and glycogen, is of considerable interest in view of the author's own extensive researches on these and related derivatives. The student will find here a valuable account of modern views on a subject of interest alike to chemist, biologist, botanist, and industrialist. To what extent some of this work is of a really permanent character, and capable of withstanding the criticism recently directed against it from various quarters, the future alone can decide.

In final sections, dealing with molecular conceptions, viscosity, molecular size, molecular cohesion, and x-ray investigations, the reader is made familiar with the general nature and results of recent important investigations. The book can be heartily recommended to all students of carbohydrate and polysaccharide chemistry. It is to be hoped that the author may see his way clear to an early revision of his well-known and valuable textbook on "Carbohydrate Chemistry" in which particular attention, let us hope, may be given to an extended and careful description of the fundamental work on which present views of the ring structure of glucose and other sugars are based. Such knowledge would prove of considerable assistance in the acquisition of a thorough grasp of the valuable information contained in the present volume. HAROLD HIBBERT

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DIE CHEMIE DER KOHLEN. *By Georg Stadnikoff.* 339 pages, 28 illustrations, 188 tables. Ferdinand Enke, Stuttgart, 1931. Price, bound, 21 marks.

IN THE words of the author, this monograph is an attempt to summarize present-day knowledge of the chemistry of coal in the form of general viewpoints and conclusions in so far as these are established by experimental evidence. The subject is introduced with two chapters on the general characteristics, origin, and metamorphism of coal, with special emphasis on peat and the early stages of coal formation. The chemistry of the plant constituents are taken up in some detail. Composition and constitution are then discussed in logical order of moisture, ash-forming constituents, sulfur, nitrogen, and organic matter. The action of organic solvents and the nature of the "bitumens" and humic matter in the various types and ranks of coal are treated at some length.

The last half of the book is devoted to primary tar, gas, and semi-coke; high-temperature tar, coke, and gas; hydrogenation of coal; classification; and oxidation of coal.

The book is written from the point of view of the organic and colloid chemist, interested in fundamental research on the constitution of coal. Throughout the text the author sticks to chemistry and does not wander afield in general technology or description of processes. The book is especially strong in dealing with the action of solvents on peat, cannels, boghead, and brown coals, and their primary distillation products, the author's extended experience in research on Russian and Siberian peat and boghead coals being reflected in the book. Unfortunately, his lack of familiarity with high-rank coals from other parts of the world has led him to greatly overemphasize sapropelic matter as a coal-forming component, and to assume that the vitrain of high-rank coals is of sapropelic origin. Another weakness of the book is the omission of most of the work of British investigators on coal constitution. The following typographical errors were noticed: reference to A. C. Fieldner is given as "A. E. Fieldner" on page 86, and "C. A. Fieldner" on pages 299 and 301; page 39, "Lifse" should be "Lisse;" page 77, "Tjiessen" should be "Thiessen;" page 245, "Burges" should be "Burgess;" page 314, "Millner" should be "Milner;" page 320, "I. D. Davis" should be "J. D. Davis."

The style of writing is clear and direct, unusually so for a German text. Although the book is of no great interest to the American industrial coal chemist, it is of decided value to the research worker, especially one who is interested in the fundamentals of coal chemistry and the characteristics of boghead types and the younger ranks of coal. A. C. FIELDNER

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DIE FABRIKATION PHARMAZEUTISCHER UND CHEMISCH-TECHNISCHER PRODUKTE. *By Julius Schwyzer.* 487 pages. Julius Springer, Berlin, 1931. Price, bound, 42 marks.

THIS is a rather unusual book. Instead of following the routine textbook procedure of giving a promiscuous compilation of methods and apparatus, and leaving the choice to the usually uninformed or insufficiently informed reader, Schwyzer presents a selection based apparently on personal, thoroughly practical experience, and dealing with both the laboratory and the technical aspects of the problems treated. The preparations discussed belong almost entirely in the group of medicinal products; the title of the book, which would seem to denote a much broader scope, is therefore hardly justified. The preparations are divided into the major groups of inorganic, aliphatic, and aromatic products, alkaloids, and miscellaneous subjects, the items of each group being given in alphabetic order. While the selective mode of presentation adopted by the author has its advantages, it also has its disadvantages, particularly as it prompts him to proceed in a rather dogmatic manner in a number of instances. Thus, for example, it is postulated that the definition of Argentum proteinicum (with which the author seems to be particularly familiar) should be "a mixture of silver-sodium hydroprotalbinate with lysalbinic acid." It is questionable whether the rather complicated procedure described is actually necessary to obtain a compound possessing the characteristics desired of a silver-protein compound. Besides, the author fails to state that the efficacy of the product depends largely upon the concentration of free metal ions, nor does he show how this variable factor can be influenced and utilized in preparing products of this type by a suitable selection of initial materials and adjustment of the manufacturing process. In spite of such shortcomings, both the student and the technological chemist in a plant which manufactures medicinal chemicals will find useful and practical ideas in this book. EMIL KLARMANN

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STATISTISCHE ZUSAMMENSTELLUNGEN ÜBER ALUMINIUM, BLEI, KUPFER, NICKEL, QUECKSILBER, SILBER, ZINK UND ZINN. 32nd annual issue, 1920–30. xxix + 91 pages, 155 × 293 cm. Metallgesellschaft Aktiengesellschaft, Frankfurt a. M., Germany, 1931.

METALLURGISTS and executives, active in the nonferrous metals industries, have become accustomed to watching for this excellent annual survey of production, consumption, import duties of the various countries, selling prices, and average prices in New York, London, and Berlin, of the metals enumerated in the title.

The introduction (9 pages), embellished with a chart for each of the metals, presents a succinct picture of the nonferrous metals industries for the past ten years, together with an illuminating exposition of their present status.

As usual, the typography and proof reading are excellent.

The book is available in this country in the Commercial Division of the Ore and Chemical Corporation, and in the Technical Division of the American Lurgi Corporation, both at 40 Rector St., New York, N. Y., which will, no doubt, be glad to forward copies to interested persons as long as their supply lasts.

D. D. BEROLZHEIMER

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In the bibliography of the review of "Creep of Metals," by H. J. Tapsell [IND. ENG. CHEM., 23, 1480 (1931)], the publisher should be simply the Oxford University Press, New York. The correct English price is 30s., and the American price has now been reduced from $12 to $10.

GOVERNMENT PUBLICATIONS

Notice. *Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate.*

BUREAU OF FOREIGN AND DOMESTIC COMMERCE

Statistical Abstract of the United States, 1931. Fifty-third Number. 898 pp. Buckram, $1.25.

BUREAU OF MINES

Abrasive Materials in 1930. Paul Hatmaker and A. E. Davis. (*Mineral Resources of the United States, 1930.*) Part II, pp. 151–69. Paper, 5 cents.

Annual Report of Director of Bureau of Mines for Fiscal Year Ended June 30, 1931. 61 pp. Paper, 10 cents.

Arsenic, Bismuth, Selenium, and Tellurium in 1930. V. C. Heikes. (*Mineral Resources of the United States, 1930.*) Part I, pp. 25–30. Paper, 5 cents.

Coal in 1929. F. G. Tryon and L. Mann. (*Mineral Resources of the United States, 1929.*) Part II, pp. 673–858. Price, 35 cents.

Explosions in Washington Coal Mines. S. H. Ash. (*Technical Paper 507.*) 52 pp. Paper, 10 cents.

Feldspar in 1930. H. H. Hughes and Jefferson Middleton. (*Mineral Resources of the United States, 1930.*) Part II, pp. 137–49. Paper, 5 cents.

Gases That Occur in Metal Mines. D. Harrington and E. H. Denny. (*Bulletin 347.*) 21 pp. Paper, 5 cents.

Gold, Silver, Copper, Lead, and Zinc in Colorado in 1929. Mine Report. C. W. Henderson. (*Mineral Resources of the United States, 1929.*) Part I, pp. 921–68. Paper, 10 cents.

Influence of Fractionation on Distribution of Sulfur in Gasoline. R. H. Espach and H. P. Rue. (*Technical Paper 505.*) 24 pp. Paper, 10 cents.

Lead and Zinc Pigments and Salts in 1930. E. W. Pehrson. (*Mineral Resources of the United States, 1930.*) Part I, pp. 113–31. Paper, 5 cents.

Methods and Apparatus Used in Determining the Gas, Coke, and By-Product Making Properties of American Coals. A. C. Fieldner, J. D. Davis, R. Thiessen, E. B. Kester, and W. A. Selvig. (*Bulletin 344.*) 107 pp. Paper, 40 cents.

Mineral Resources of the United States, 1930 (Summary). O. E. Kiessling and M. B. Clark. 120 pp. Paper, 20 cents.

Platinum and Allied Metals in 1930. H. W. Davis. (*Mineral Resources of the United States, 1930.*) Part I, pp. 99–112. Paper, 5 cents.

Sulfur and Pyrites in 1930. R. H. Ridgway. (*Mineral Resources of the United States, 1930.*) Part II, pp. 117–35. Paper, 5 cents.

Survey of Fuel Consumption at Refineries in 1930. G. R. Hopkins. (*Reports of Investigations 3145.*) 12 pp.

Vanadium, Uranium, and Radium. F. L. Hess. (*Mineral Resources of the United States, 1930.*) Part I, pp. 133–50. Paper, 5 cents.

BUREAU OF STANDARDS

Annual Report of Director of Bureau of Standards for Fiscal Year Ended June 30, 1931. (*Miscellaneous Publication 131.*) 50 pp. Paper, 15 cents.

A Survey of Storage Conditions in Libraries Relative to the Preservation of Records. A. E. Kimberly and J. F. G. Hicks, Jr. (*Miscellaneous Publication 128.*) 8 pp. Paper, 5 cents.

Properties of Fiber Building Boards. C. G. Weber, F. T. Carson, and L. W. Snyder. (*Miscellaneous Publication 132.*) 14 pp. Paper, 5 cents.

The Resistance to Wear of Carbon Steels. S. J. Rosenberg. (*Research Paper 348.*) 10 pp. Paper, 10 cents.

From *Bureau of Standards Journal of Research*

A General Formula for the Computation of Colorimetric Purity. Deane B. Judd. 7 (November, 1931), 827–41.

Derivatives of 4-Glucosido-Mannose. H. S. Isbell. 7 (December, 1931), 1115–31.

Determination of Insoluble Matter in Shellac. C. C. Hartman. 7 (December, 1931), 1105–13.

Highly Purified Wood Fibers as Paper-Making Material. Royal H. Rasch, Merle B. Shaw, and George W. Bicking. 7 (November, 1931), 765–82.

Isolation and Determination of Methylcyclopentane in a Midcontinent Petroleum. M. M. Hicks-Bruun and J. H. Bruun. 7 (November, 1931), 799–809.

Isolation of Normal Nonane from a Midcontinent Petroleum. Joseph D. White and F. W. Rose, Jr. 7 (November, 1931), 907–11.

Laboratory Rectifying Stills of Glass. J. H. Bruun and S. T. Schicktanz. 7 (November, 1931), 851–82.

Silvering and Evacuating Pyrex Dewar Flasks. R. B. Scott, J. W. Cook, and F. G. Brickwedde. 7 (November, 1931), 935–43.

Tests of Integral and Surface Waterproofings for Concrete. C. H. Jumper. 7 (December, 1931), 1147–77.

The Analysis of Cyanide Silver-Plating Solutions. R. M. Wick. 7 (November, 1931), 913–33.

The Decomposition of Tricalcium Silicate in the Temperature Range, 1000–1300° C. E. T. Carlson. 7 (November, 1931), 893–902.

The Determination of the Coefficient of Cubical Expansion of Solid Benzoic Acid by Means of a Gas-Filled Dilatometer. E. R. Smith. 7 (November, 1931), 903–5.

The Effect of pH on the Photochemical Decomposition of Silk. Milton Harris and Daniel A. Jessup. 7 (December, 1931), 1179–84.

The Use of Zinc Oxide in Determinations of Cobalt and Manganese. James I. Hoffman. 7 (November, 1931), 883–92.

Thermal Expansion of Heat-Resisting Alloys: Nickel-Chromium, Iron-Chromium, and Nickel-Chromium-Iron Alloys. Peter Hidnert. 7 (December, 1931), 1031–66.

Thermal Expansions of Gasolines from 0–30° C. C. S. Cragoe and E. E. Hill. 7 (December, 1931), 1133–45.

DEPARTMENT OF AGRICULTURE

Buckwheat Milling and Its By-Products. M. R. Coe. (*Circular 190.*) 12 pp. Paper, 5 cents.

Fertilizers for Cotton Soils. J. J. Skinner. (*Miscellaneous Publication 126.*) 10 pp. Paper, 5 cents.

Report of Chief of Bureau of Chemistry and Soils. 78 pp. Paper, 10 cents.

Report of Chief of Food and Drug Administration. 30 pp. Paper, 5 cents.

Report of the Secretary of Agriculture, 1931. 102 pp.

Review of United States Patents Relating to Pest Control. R. C. Roark. 4, No. 10 (October, 1931), 10 pp. Paper, 10 cents.

Same. No. 11 (November, 1931), 9 pp. Paper, 10 cents.

From *Journal of Agricultural Research*

Changes in the Chemical Composition of Mangels and Rutabagas during Storage. K. S. Morrow, R. B. Dustman, and H. O. Henderson. 43 (November 15, 1931), 919–30.

Nonprotein Nitrogen of the Alaska Pea, with Special Reference to the Chemical Nature of Humin Nitrogen. S. L. Jodidi. 43 (November 1, 1931), 811–25.

Oleoresin Production from Longleaf Pine Defoliated by Fire. Eloise Gerry. 43 (November 1, 1931), 827–36.

The Percentage of Fat as a Basis for Estimating the Composition of Milk. Orme J. Kahlenberg and Le Roy Voris. 43 (October 15, 1931), 749–55.

GEOLOGICAL SURVEY

Annual Report of Director of Geological Survey for the Fiscal Year Ended June 30, 1931. 95 pp. Paper, 15 cents.

Mineral Industry of Alaska in 1930 and Administrative Report. P. S. Smith. (*Bulletin 836-A.*) 115 pp. Paper, 20 cents.

Origin and Microfossils of the Oil Shale of the Green River Formation of Colorado and Utah. W. H. Bradley. (*Professional Paper 168.*) 58 pp. Paper, 60 cents.

Shorter Contributions to General Geology, 1930. W. C. Mendenhall. (*Professional Paper 165.*) 180 pp. Paper, $1.25.

Surface Water Supply of the United States, 1929. Part XII. North Pacific Slope Drainage Basins. B. Snake River Basin. N. C. Grover and Others. (*Water-Supply Paper 693.*) 183 pp. Paper, 30 cents.

Surface Water Supply of the United States, 1930. Part X. The Great Basin. N. C. Grover and Others. (*Water-Supply Paper 705.*) 92 pp. Paper, 20 cents.

MARKET REPORT—JANUARY, 1932

THESE PRICES UNLESS OTHERWISE SPECIFIED ARE THOSE PREVAILING IN THE NEW YORK MARKET, JANUARY 15, FOR COMMERCIAL GRADES IN CARLOAD QUANTITIES

Newer Chemicals

Acetaldehyde, drums, lc-l., wks.	lb.	.18½
Acetaldol, 50-gal. drums	lb.	.27
Acetylene tetrachloride, *see* Tetrachloroethane		
Acid, abietic	lb.	.12
Adipic	lb.	.72
Linoleic	lb.	.16
Ammonium linoleate, drums	lb.	.15
Amyl furoate, 1-lb. tins	lb.	5.00
Aroclors	lb.	.40
Butyl carbitol, *see* Diethylene glycol monobutyl ether		
Cellosolve, *see* Ethylene glycol monobutyl ether		
Furoate, tech., 50-gal. drums	lb.	1.00
Carbitol, *see* Diethylene glycol monoethyl ether		
Cellosolve, *see* Ethylene glycol monoethyl ether		
Acetate, *see* Ethylene glycol monoethyl ether acetate		
Crotonaldehyde, 50-gal. drums	lb.	.32
Dichloroethyl ether, 50-gal. drums	lb.	.06
Diethylene glycol, drums	lb.	.14
Monobutyl ether, drums	lb.	.24
Monoethyl ether, drums	lb.	.15
Diethylene oxide, 50-gal. drums	lb.	.50
Dioxan, *see* Diethylene oxide		
Diphenyl	lb.	.30
Ethyl acetoacetate, 50-gal. drums	lb.	.65
Carbonate, 90%, 50-gal. drums	gal.	1.85
Chlorocarbonate, carboys	lb.	.30
Ether, absolute, 50-gal. drums	lb.	.50
Furoate, 1-lb. tins	lb.	5.00
Ethylene chlorhydrin, 40%, 10-gal. cbys	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.	.19½
Monomethyl ether, drums	lb.	.21
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
Glyceryl phthallate	lb.	.26
Glycol stearate	lb.	.18
Isopropyl ether, drums	lb.	.10
Lead dithiofuroate, 100-lb. drums	lb.	1.00
Magnesium peroxide, 100-lb. cs.	lb.	1.15
Methyl acetate, drums	gal.	1.20
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.	.20
Propyl furoate, 1-lb. tins	lb.	2.50
Strontium peroxide, 100-lb. drums	lb.	1.25
Sulfuryl chloride, 600-lb. drums, crude	lb.	.15
Distilled	lb.	.40
Tetrachloroethane, 50-gal. drums	lb.	.09
Trichloroethylene, 50-gal. drums	lb.	.10
Triethanolamine, 50-gal. drums	lb.	.40
Trihydroxyethylamine linoleate	lb.	.40
Trihydroxyethylamine stearate	lb.	.35
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., powd., bbls.	lb.	.24
Acetic anhydride, 92–95%, cbys.	lb.	.21
Acetone, drums, wks.	lb.	.10¼
Acetphenetidin, bbls.	lb.	1.25
Acid, acetic, 28%, c/l., bbls.	100 lbs.*	2.40
56%, c/l., bbls.	100 lbs.	4.60
Glacial, c/l., bbls.	100 lbs.	8.10
Glacial, U. S. P., c/l., carboys	100 lbs.	8.85
Acetylsalicylic, bbls.	lb.	.75
Anthranilic, 99–100%, drums	lb.	.85
Benzoic, tech., bbls.	lb	.40
Boric, bbls.	lb.	.06⅓
Butyric, 100% basis, cbys.	lb.	.80
Chloroacetic, mono-, bbls., wks.	lb.	.18
Di-, cbys.	lb.	1.00
Tri-, bbls.	lb.	2.50
Chlorosulfonic, drums, wks.	lb.	.04½
Chromic, 99%, drums	lb.	.13¼
Cinnamic, bottles	lb.	3.25
Citric, U. S. P., cryst., bbls.	lb.	.33½
Cresylic, pale, drums	gal.	.49
Formic, 90%, cbys., N. Y.	lb.	.10¼
Gallic, U. S. P., bbls.	lb.	.74
Glycerophosphoric, 25%, 1-lb. bot.	lb.	1.40
H, bbls., wks.	lb.	.65
Hydriodic, 10%, U. S. P., 5-lb. bot.	lb.	.67
Hydrobromic, 48%, cbys., wks.	lb	.45
Hydrochloric, 20°, tanks, wks.	100 lbs.	1.35
Hydrofluoric, 30%, bbls., wks.	lb.	.06
60%, bbls., wks.	lb.	.13
Hydrofluosilic, 35%, bbls., wks.	lb.	.11
Hypophosphorus, 30%, U. S. P., 5-gal. demis.	lb.	.85
Lactic, 22%, dark, bbls.	lb.	.04
48%, light, bbls., wks.	lb.	.11
Mixed, tanks, wks.	N unit	.07
	S unit	.08
Molybdic, 85%, kegs	lb.	1.25
Naphthionic, tech., bbls.	lb.	nom.
Nitric, C. P., cbys.	lb.	.11
Nitric, 36°, c/l., cbys., wks.	100 lbs.	5.00
Oxalic, bbls., wks.	lb.	.11
Phosphoric, 50%, U. S. P.	lb.	.14
Picramic, bbls.	lb.	.65
Picric, bbls., c/l.	lb.	.30
Pyrogallic	lb.	1.50
Salicylic, tech., bbls.	lb.	.33
Stearic, d. p., bbls., c/l.	lb.	.08
Sulfanilic, 250-lb. bbls.	lb.	.15
Sulfuric, 66°, c/l., cbys., wks.	100 lbs.	1.60
66°, tanks, wks.	ton	15.00
60°, tanks, wks.	ton	10.50
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.	.23
Tartaric, U. S. P., cryst., bbls.	lb.	.25½
Tungstic, kegs	lb.	1.40
Valeric, C. P., 10-lb. bot.	lb.	2.50
Alcohol, U. S. P., 190 proof, bbls.	gal.	2.57
Amyl, from pentane, tanks	lb.	.203
Amyl, Imp. drums	gal.	1.75
Butyl, drums, c/l., wks.	lb.	.148
Cologne spirit, bbls.	gal.	2.69
Denatured, No. 5, comp. denat., c/l., drums	gal.	.34½
Isoamyl, drums	gal.	4.00
Isobutyl, ref., drums	gal.	1.00
Isopropyl, ref., drums	gal.	.60
Propyl, ref., drums	gal.	1.00
Wood, *see* Methanol		
Alpha-naphthol, bbls.	lb.	.73
Alpha-naphthylamine, bbls.	lb.	.32
Alum, ammonia, lump, bbls., wks.	100 lbs.	3.30
Chrome, casks, wks.	100 lbs.	5.00
Potash, lump, bbls., wks.	100 lbs.	3.35
Soda, bbls., wks.	100 lbs.	3.45
Aluminum, metal, N. Y.	ton	22.90
Aluminum chloride, anhyd., commercial, wks., drums extra, c/l.	lb.	.05
Aluminum stearate, 100-lb. bbl.	lb.	.20
Aluminum sulfate, comm'l, bags, wks.	100 lbs.	1.25
Iron-free, bags, wks.	100 lbs.	1.90
Aminoazobenzene, 100-lb. kegs	lb.	1.15
Ammonia, anhydrous, cyl., wks.	lb.	.15½
50,000-lb. tanks, wks.	lb.	.05625
Ammonia, aqua, 26°, tanks, wks., contained NH_3	lb.	.05½
Ammonium acetate, kegs	lb.	.33
Bifluoride, bbls.	lb.	.21
Bromide, 50-lb. boxes	lb.	.35
Carbonate, tech., casks	lb.	.08
Chloride, gray, bbls.	100 lbs.	5.25
Lump, casks	lb.	.10½
Iodide, 25-lb. jars	lb.	5.20
Nitrate, tech., cryst., bbls.	lb.	.08½
Oxalate, kegs	lb.	.22
Persulfate, cases	lb.	.26
Phosphate, dibasic, tech., bbls.	lb.	.10¾
Sulfate, bulk, wks.	100 lbs.	1.10
Amyl acetate, tech., from pentane, tanks	lb.	.175
Aniline oil, drums	lb.	.14½
Anthracene, 80–85%, casks, wks.	lb.	.60
Anthraquinone, subl., bbls.	lb.	.50
Antimony, metal	lb.	.06⅛
Antimony chloride, drums	lb.	.13
Oxide, bbls.	lb.	.08½
Salt, dom., bbls.	lb.	.22
Sulfide, crimson, bbls.	lb.	.25
Golden, bbls.	lb.	.16
Vermilion, bbls.	lb.	.38
Argols, red powder, bbls.	lb.	.07
Arsenic, metal, kegs	lb.	.30
Red, kegs, cases	lb.	.09⅜
White, c/l., kegs	lb.	.04
Asbestine, bulk, c/l.	ton	15.00
Barium carbonate, bbls., bags, wks.	ton	56.50
Chloride, bbls., wks.	lb.	.03¾
Dioxide, drs., wks.	lb.	.12
Hydroxide, bbls.	lb.	.05¼
Nitrate, casks	lb.	.07¼
Barium thiocyanate, 400-lb. bbls.	lb.	.27
Barytes, floated, 350-lb. bbls., wks.	ton	23.00
Benzaldehyde, tech., drums	lb.	.60
F. F. C., cbys.	lb.	1.40
U. S. P., cbys.	lb.	1.15
Benzidine base, bbls.	lb.	.65
Benzol, tanks, wks.	gal.	.20
Benzoyl chloride, cbys.	lb.	1.00
Benzyl acetate, F. F. C., bottles	lb.	.75
Alcohol, 5-liter bot.	lb.	1.20
Chloride, tech., drums	lb.	.30
Beta-naphthol, bbls.	lb.	.22
Beta-naphthylamine, bbls.	lb.	.58
Bismuth, metal, cases	lb.	1.00
Bismuth, nitrate, 25-lb. jars	lb.	.95
Oxychloride, boxes	lb.	2.95
Subnitrate, U. S. P., 25-lb. jars	lb.	1.20
Blanc fixe, dry, bbls.	ton	70.00
Bleaching powder, drums, wks.	100 lbs.	2.00
Bone ash, kegs	lb.	.06
Bone black, bbls.	lb.	.08¼
Borax, bags	lb.	.02½
Bordeaux mixture, bbls.	lb.	.11½
Bromine, bot.	lb.	.36
Bromobenzene, drums	lb.	.50
Bromoform, jars	lb.	1.80
Butyl acetate, drums, c/l.	lb.	.159
Cadmium bromide, 50-lb. jars	lb.	1.40
Cadmium, metal, cases	lb.	.55

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* Contract price.

Cadmium sulfide, boxes	lb.	.60
Caffeine, U. S. P., 5-lb. cans	lb.	2.40
Calcium acetate, bags	100 lbs.	2.00
Arsenate, bbls	lb.	.06
Carbide, drums	lb.	.05½
Chloride, drums, wks., flake	ton	21.00
Cyanide, 100-lb. drums	lb.	.30
Nitrate, bags	ton	35.00
Phosphate, monobas., bbls	lb.	.08
Tribas., bbls	lb.	.11
Calcium carbonate, tech., bags,	100 lbs.	1.00
U. S. P., precip., 175-lb. bbl	lb.	.06½
Camphor, Jap., cases	lb.	.49
Carbazole, bbls	lb.	.75
Carbon, activated, drums	lb.	.08
Carbon bisulfide, drums	lb.	.05
Carbon black, cases	lb.	.06
Carbon dioxide, liq. cyl	lb.	.06
Carbon tetrachloride, drums	lb.	.06¼
Casein, stand. gr., bbls	lb.	.07
Cellulose acetate, bbls	lb.	.80
Cerium oxalate, kegs	lb.	.33
Charcoal, willow, powd., bbls	lb.	.06
China clay, bulk	ton	8.00
Chloral hydrate, drums	lb.	.70
Chlorine, liq., c/l., cyl	lb.	.04
Chlorine, tanks	100 lbs.	1.75
Chlorobenzene, mono-, drums	lb.	.10
Chloroform, tech., drums	lb.	.15
Chromium acetate, 20° soln., bbls.	lb.	.05
Coal tar, bbls., wks	gal.	.10
Cobalt, metal, kegs	lb.	2.50
Cobalt oxide, bbls	lb.	1.35
Cod-liver oil, bbls	bbl.	30.00
Copperas, c/l., bulk	ton	14.50
Copper, metal, elec	100 lbs.	7.25
Copper carbonate, bbls., 52/54%	lb.	.16½
Chloride, bbls	lb.	.22
Cyanide, drums	lb.	.39
Oxide, red, bbls	lb.	.15½
Sulfate, c/l., bbls	100 lbs.	3.10
Cotton, soluble, bbls	lb.	.40
Cream tartar, bbls	lb.	.20¼
Cyanamide, bulk, N. Y.	Ammonia unit	.97½
Diaminophenol, kegs	lb.	3.80
Dianisidine, bbls	lb.	2.35
Dibutylphthalate, drums, wks	lb.	.22⅘
Diethylaniline, drums	lb.	.55
Diethylene glycol, drums	lb.	.14
Diethyl phthalate, drums	lb.	.23
Diethyl sulfate, tech., drums	lb.	.30
Dimethylaniline, drums	lb.	.26
Dimethylsulfate, drums	lb.	.45
Dinitrobenzene, drums	lb.	.15½
Dinitrochlorobenzene, bbls	lb.	.13
Dinitronaphthalene, bbls	lb.	.34
Dinitrophenol, bbls	lb.	.29
Diphenylamine, bbls	lb.	.37
Diphenylguanidine, bbls	lb.	.30
Epsom salt, tech., bbls., c/l., N. Y.	100 lbs.	1.70
Ether, nitrous, bot	lb.	.80
Ether, U. S. P., drums	lb.	.09
Ethyl acetate, tanks, c/l	lb.	.09
Bromide, drums	lb.	.50
Chloride, drums	lb.	.22
Methyl ketone, drums	lb.	.30
Ethylbenzylaniline, 300-lb. drums	lb.	.88
Ethylene dichloride	lb.	.05
Chlorohydrin, anhyd., drums	lb.	.75
Glycol, c/l., wks	lb.	.25
Feldspar, bulk	ton	6.50
Ferric chloride, tech., bbls	lb.	.05
Ferrous chloride, cryst., bbls	lb.	.06
Ferrous sulfide, bbls	100 lbs.	2.50
Fluorspar, 98%, bags	ton	31.00
Formaldehyde, bbls	lb.	.06
Formaniline, drums	lb.	.37½
Fuller's earth, bags, c/l., mines	ton	15.00
Furfural drums, tech., contract, works	lb.	.10
Glauber's salt, bbls	100 lbs.	1.00
Glucose, 70°, bags, dry	100 lbs.	3.14
Glycerine, c. p., drums	lb.	.11¼
G salt, bbls	lb.	.42
Hexamethylenetetramine, tech., drums	lb.	.46
Hydrogen peroxide, 25 vol., bbls.	lb.	.05½
Hydroquinone, kegs	lb.	1.20
Indigo, 20%, paste, bbls	lb.	.12
Iodine, crude, 200-lb. kgs	lb.	4.20
Iodine, resubl., jars	lb.	4.65
Iodoform, bot	lb.	6.00
Iridium, metal	oz.	160.00
Kieselguhr, bags	ton	50.00
Lead, metal, N. Y	100 lbs.	3.75
Lead acetate, bbls., white	lb.	.11
Arsenate, bbls	lb.	.10
Oxide, litharge, bbls	lb.	.05¾
Peroxide, drums	lb.	.20
Red, bbls	lb.	.06¾
Sulfate, bbls	lb.	.06½
White, basic carb., bbls	lb.	.07¼
Lime, hydrated, bbls	100 lbs.	.85
Lime, live, chemical, bbls., wks.	100 lbs.	1.05
Limestone, ground, bags, wks	ton	4.50
Lithopone, bbls	lb.	.04½
Magnesite, crude	ton	32.00
Calcined, 500-lb. bbls., wks	ton	40.00
Magnesium, metal, wks	lb.	.30
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.	.07½
Dioxide, 80%, bbls	ton	80.00
Sulfate, casks	lb.	.07
Mercury bichloride, cryst., 50 lbs.	lb.	1.59
Mercury, flasks, 76 lbs	flask	67.00
Meta-nitroaniline, bbls	lb.	.67
Meta-phenylenediamine, bbls	lb.	.80
Meta-toluylenediamine, bbls	lb.	.67
Methanol, pure, synthetic, drums, wks	gal.	.37½
Tanks, wks	gal.	.35½
Methyl acetone, drums	gal.	.50
Salicylate, cases	lb.	.42
Methyl chloride, cylinders	lb.	.45
Michler's ketone, bbls	lb.	3.00
Naphtha, solvent, tanks	gal.	.26
Naphthalene, flake, bbls	lb.	.03¾
Nickel, metal	lb.	.35
Nickel salt, single, bbls	lb.	.10
Double, bbls	lb.	.10
Niter cake, bulk	ton	12.50
Nitrobenzene, drums	lb.	.08½
Oil, castor, No. 1	lb.	.10
China wood, bbls	lb.	.06½
Coconut, Ceylon, tanks	lb.	.03⅜
Cod, N. F., tanks	gal.	.25
Corn, crude, tanks, mills	lb.	.03¼
Cottonseed, crude, tanks	lb.	.04
Lard, edible, bbls	lb.	.11¼
Linseed, bbls	lb.	.071
Menhaden, crude, tanks	gal.	.20
Neat's-foot, pure, bbls	lb.	.09½
Oleo, No. 1, bbls	lb.	.07¼
Olive oil, denat., bbls	gal.	.63
Foots, bbls	lb.	.04⅜
Palm, Lagos, casks	lb.	.04⅛
Peanut, crude, bbls	lb.	.07
Perilla, bbls	lb.	.06½
Rapeseed, bbls., English	gal.	.39
Red, bbls	lb.	.06⅝
Soy bean, crude, bbls	lb.	.046
Sperm, 38°, bbls	gal.	.68
Whale, bbls., natural, winter	gal.	.58
Ortho-aminophenol, kegs	lb.	2.15
Ortho-dichlorobenzene, drums	lb.	.08
Ortho-nitrochlorobenzene, drums	lb.	.28
Ortho-nitrophenol, bbls	lb.	.85
Ortho-nitrotoluene, drums	lb.	.16
Ortho-toluidine, bbls	lb.	.20
Palladium, metal	oz.	19.00
Para-aminophenol, kegs	lb.	.84
Para-dichlorobenzene	lb.	.15½
Para-formaldehyde, cases	lb.	.38
Paraldehyde, tech., drums	lb.	.20½
Para-nitraniline, drums	lb.	.48
Para-nitrochlorobenzene, drums	lb.	.25
Para-nitrophenol, bbls	lb.	.45
Para-nitrosodimethylaniline, bbls	lb.	.92
Para-nitrotoluene, bbls	lb.	.29
Para-phenylenediamine, bbls	lb.	1.15
Para-toluidine, bbls	lb.	.40
Paris Green, 250-lb. kegs	lb.	.25
Phenol, drums	lb.	.14¼
Phenolphthalein, drums	lb.	.80
Phenylethyl alcohol, 1-lb. bot	lb.	7.00
Phosphorus, red, cases	lb.	.45
Phosphorus trichloride, cyl	lb.	.35
Phthalic anhydride, bbls	lb.	.15
Platinum, metal	oz.	38.00
Potash, caustic, drums	lb.	.06⅛
Potassium acetate, kegs	lb.	.28
Bicarbonate, casks	lb.	.09½
Bichromate, casks	lb.	.08
Binoxalate, bbls	lb.	.14
Bromate, cs	lb.	.35
Carbonate, 80–85%, calc., casks	lb.	.04¾
Chlorate, kegs	lb.	.08
Chloride	ton	34.55
Cyanide, cases	lb.	.55
Meta-bisulfite, bbls	lb.	.11
Permanganate, drums	lb.	.16
Prussiate, red, casks	lb.	.37½
Yellow, casks	lb.	.18½
Titanium oxalate, bbls	lb.	.21
Pyridine, drums	gal.	1.50
Resorcinol, tech., kegs	lb.	.65
Rochelle salt, bbls., U. S. P	lb.	.16
R salt, bbls	lb.	.42
Saccharin, cans	lb.	1.70
Salt cake, bulk	ton	14.00
Saltpeter, gran., bbls	lb.	.06
Silica, ref., bags	ton	22.00
Silver nitrate, 16-oz. bot	oz.	.24¼
Soda ash, 58%, light, bags, contract, wks	100 lbs.	1.15
Soda, caustic, 76%, solid, drums, contract, wks	100 lbs.	2.50
Sodium acetate, bbls	lb.	.04½
Benzoate, bbls	lb.	.42
Bicarbonate, bbls	100 lbs.	1.85
Bichromate, casks	lb.	.05
Bisulfite, bbls	lb.	.04
Bromide, bbls., U. S. P	lb.	.31
Chlorate, kegs	lb.	.05¾
Chloride, bags	ton	12.00
Cyanide, cases	lb.	.16½
Fluoride, bbls	lb.	.07
Metallic, drums, 12¼-lb. bricks	lb.	.19
Naphthionate, bbls	lb	.52
Nitrate, crude, 200-lb. bags, N. Y	100 lbs.	1.76½
Nitrite, bbls	lb.	.07
Perborate, bbls	lb.	.18
Peroxide, cases	lb.	.21
Phosphate, trisodium	100 lbs.	3.20
Picramate, kegs	lb.	.69
Prussiate, bbls	lb.	.11½
Silicate, drums, tanks, 40°	100 lbs.	.75
Silicofluoride, bbls	lb.	.05¼
Stannate, drums	lb.	.18
Sulfate, anhyd., bbls	lb.	.02
Sulfide, cryst., bbls	lb.	.02½
Solid, 60%	lb.	.03½
Sulfocyanide, bbls	lb.	.28
Thiosulfate, reg., cryst., bbls	lb.	.02½
Tungstate, kegs	lb.	.70
Strontium carbonate, tech., bbls.	lb.	.07¼
Nitrate, bbls	lb.	.09
Sulfur, bulk, mines, wks	ton	18.00
Sulfur chloride, red, drums	lb.	.05
Yellow, drums	lb.	.03½
Sulfur dioxide, commercial, cyl	lb.	.07
Sulfuryl chloride, drums	lb.	.10
Thiocarbanilid, bbls	lb.	.26½
Tin	lb.	.21¾
Tin tetrachloride, anhydrous, drums, bbls	lb.	.16½
Oxide, bbls	lb.	.23½
Titanium dioxide, bbls., wks	lb.	.21
Toluene, tanks	gal.	.30
Tribromophenol, cases	lb.	1.10
Triphenylguanidine, drums	lb.	.58
Triphenyl phosphate, bbls	lb.	.60
Tungsten, powder	lb.	1.65
Urea, pure, cases	lb.	.11
Whiting, bags	100 lbs.	1.00
Xylene, 10°, tanks, wks	gal.	.26
Xylidine, drums	lb.	.36
Zinc, metal, E. St. Louis	100 lbs.	3.42½
Zinc ammonium chloride, bbls	lb.	.05½
Chloride, granulated, drums	lb.	.05¾
Oxide, Amer., bbls	lb.	.06½
Stearate, bbls	lb.	.20
Zinc dust, bbls., c/l	lb.	.06

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XYLOL, 3°, N.C.	76 Min.
XYLOL, 5°, N.C.	81 Min.
XYLOL, 10°, N.C.	89 Min.
Amyl Acetate	90 Min.
XYLOL, INDUSTRIAL	108 Min.
CRUDE LIGHT SOLVENT NAPHTHA	126 Min.
V.M.P. Naphtha	175 Min.
HI-FLASH NAPHTHA 185° END POINT	310 Min.
HI-FLASH NATHTHA 195° END POINT	360 Min.
Turpentine	450 Min.
HEAVY NAPHTHA, E.W.	1440-1500 Min.

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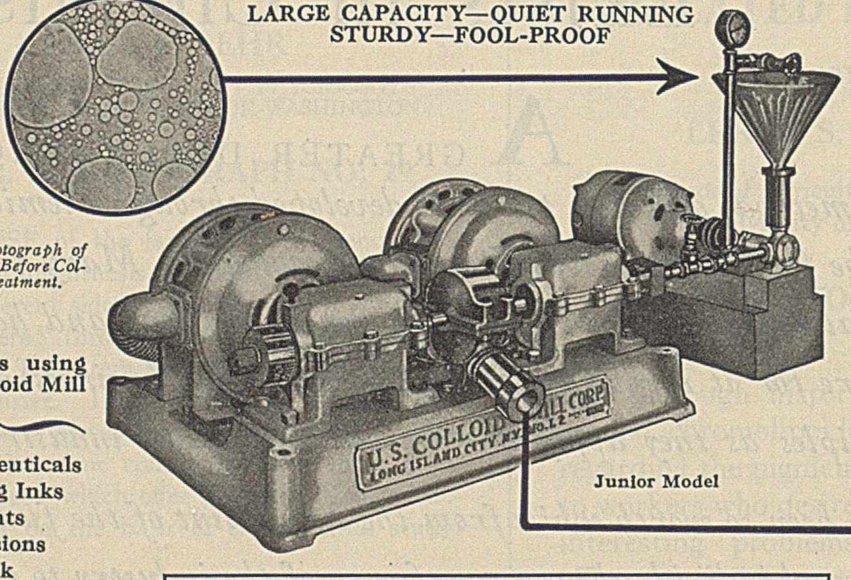

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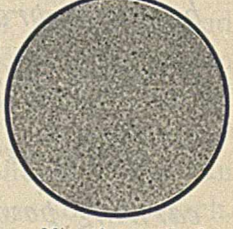

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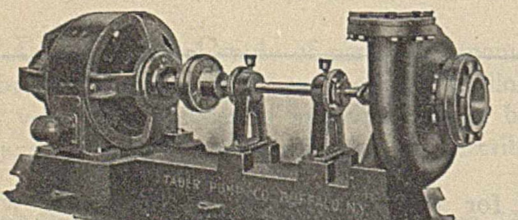

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