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The Editor's Point of View

WHAT OF CHEMISTRY AND CHEMISTS IN AMERICA? A new year is upon us. What of chemistry and chemists in America? To the promotion of their welfare our Society stands committed. Have we builded well for future achievement?

What seem to be the facts?

We have greater wealth than ever before; wealth to endow education and research in the pure science; wealth to finance industrial research and its exploitation.

Men of finance, industry, and commerce are becoming more and more research-conscious.

We have a broadening foundation of knowledge on which to build; an expanding, inexhaustible territory to be explored and cultivated.

We have a greater number of well-trained workers.

True, we have much to learn about the control of wealth, whether of labor or of commodities. We have not learned to achieve economic stability. But in terms of living, every crest of the wave has been higher and every trough less depressed. We are reassured by the fact that our present condition is one of maladjustment, not poverty; surfeit, not famine.

The man of business may be getting a dangerously exalted estimate of the possibilities of research. He will come to learn its limitations. His interest will grow; the results will compel it.

In the early days of science there were those who believed its domain to be narrowly bounded. Few today do not see its horizons receding with every advance.

Years ago we were told that there would soon be an oversupply of men trained in chemistry. Some fear that such fate is now upon us. But before these days of doubt and uncertainty the schools were not keeping up with the demand for men of good training. Today, discouraging as is the immediate outlook for many, the proportion of those who are idle is, to say the least, no higher among chemists than among those in other walks of life. We shall again have a scarcity of well-trained men.

Science properly taught is as cultural as the humanities. A foundation of training in chemistry and the allied sciences is of value in all walks of life. It is neither necessary nor desirable that all men trained in science practice a scientific calling. The need is for leaders in finance, industry, and commerce who understand the possibilities and the limitations of modern science.

What with our increasing wealth, the growing appreciation of the value of research, our ever expanding knowledge, the increasing number of men of power and initiative who are devoting their lives to chemistry or its practical application, the future of chemistry and chemists in America never looked brighter.

L. V. Redman

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THE BANKER—A FALLEN IDOL. In the new National Museum at Washington, in a corner not reached by all visitors, is a collection of bronzes by Herbert Ward. This is a magnificent group, depicting a few of the primitive people of Africa, and includes "The Idol Maker." This shows a workman in perfectly natural attitude with a block of wood held over his knee, as he carves.

Most of us are idol makers, though we work in a different medium and with a somewhat different objective. The banker has long been an idol. He dominates many a community and his advice has been sought with the same appreciation of its value as that given by the local judge and the minister of the church. Few stop to wonder by what process of contact with other people's money our friend the banker came to possess superhuman qualities. He has been treated as if he possessed them, and from the way in which in later years he has assumed knowledge superior to others in the management of all manner of affairs it would almost seem that he believed such to be the case.

We all know the danger of general statements. And whatever may be said concerning the banking fraternity as a whole, we recognize that there are to be found individuals who, through all that has happened, have remained sane and have displayed sound judgment. Unfortunately, their number has been few and there have been cases where circumstances beyond their control have placed some of these estimable gentlemen in a very unwelcome light.

"Consult your banker" has long been a formula for meeting all manner of situations. Not so long ago some one noted a placard in one New York bank reading "before buying worthless securities elsewhere, consult our list." The English language is funny at times, isn't it?

The banks have had lists enough. The layman finds it difficult to distinguish between banks, as he has conceived them to be, and houses of issue and so-called investment companies. The prospect of quick profits through commissions has been too alluring. And now come famous bankers before congressional committees, testifying to the soundness of their institutions because, among other things, they hold comparatively few of the questionable foreign "securities." These are in the hands of their trusting customers. Somehow we remember the superior air displayed by bankers toward those who urged buying real estate in Florida, not for development, but for the quick turnover and a profit. Has the banker been a mere retailer?

While some bankers have interests so broad as to make them really ineffective in any one line, others manifestly fail to keep in touch with modern events. A banker of some prominence in his locality accosted a reporter friend of ours and told him that he had just learned of an astounding development which he thought the reporter should investigate at once, for it would surely lead to a marvelous story for his paper. It developed that the piece of news the banker had just picked up was that Russia is working on a five-year plan—and this, within the last three months!

When the prices of commodities fell sharply, it was the bankers in many cases who urged retailers to borrow to buy goods for stock. When, to their amazement, commodity values sank still lower, these same bankers became panicky, demanded their money, and forced sales, which practically dumped merchandise upon the market and helped further to demoralize wholesale and retail trade.

On the boards of various corporations are to be found representatives of the banking fraternity, and in some cases these boards authorized enormous bonuses for certain executives, already overpaid. The payment of such bonuses has constituted a drain upon funds which it is now recognized could be more properly and profitably used in other directions, but the movement for reform has started in other quarters. These same boards have also authorized stock issues, usually based on the prices established through speculation on stock exchanges, rather than upon earnings or increase in assets. Once issued, these stocks are capital just as sacred as the original issues and remain to become a burden or even an embarrassment when business is curtailed. Dividends paid in stock may easily fall into this class, and surely the enormous fees paid in stocks to organizers and as commissions in the case of mergers and purchases constitute another load for the corporation.

Our financiers are also responsible for the fallacy under which many an industrial enterprise has been launched and maintained—namely, the idea of a permanent bonded indebtedness. In some cases apparently no effort is ever made to pay bonds, and everyone is supposed to be happy if the interest is regularly forthcoming. It often happens that equipment, to purchase which bonds were sold, is worn out and discarded or becomes obsolete and inefficient, but the bonds go on forever. The practice of writing off equipment at the earliest date is quite foreign to some of our commercial enterprises, and it is no wonder that they find difficulty in maintaining themselves in satisfactory condition in the circumstances of today.

Obsolescence is another handicap often promoted by banking methods. There have been instances where equipment should have been sold to make way for better machinery but, since it stood as security for certain bank loans, if sold the proceeds had to be applied on the loan. In the absence of an appreciation of things technical, the banker could not be persuaded of the advantage to the industry involved in the transaction, with the result that the old machines had to be retained. It would be interesting to know to what extent such a situation accounts for the considerable number of obsolete plants which today constitute millstones about the neck of industry.

And then there are the foreign loans. Before the appearance of the articles by Garet Garrett which were reprinted by the Chemical Foundation, Inc., keen observers returning from Europe gave us their opinions on the use of American money in foreign lands and made remarks about the sagacity of our international bankers which it would be just as well not to repeat here. Anyone who has not read these discussions should do so speedily, for they touch upon topics of vital interest to each one of us.

Long ago we indicated what a two-edged sword such loans could be. Much of the money went into equipping industries, the better to compete with our own. The repayment of these loans may depend upon trade, possible only with reduced tariff protection, leaving our own industries and their workers to foot the bill.

But if any one thing irritates the technical man more than another, it has been the actual opposition which has developed in some places toward technical advice. Even some of our biggest banking institutions have declined to keep permanently on their staff men capable of giving them sound technical reports. For the sake of accounting they preferred to charge the cost of such advice against each particular case and to call in consultants accordingly. The result—that they would overlook some of the instances where the opinion was needed most—was inevitable. Even where given, the advice is not always heeded. Published chemical advice apparently prevented some fifteen million dollars in nitrate bonds being unloaded upon the American public. We do not know whether the failure to sell them is due to some pang of conscience, which prevented unloading upon a gullible public, or whether the customary buyers displayed better judgment than the bankers.

In a western city one of the smaller banks, with but twenty-seven vice presidents, stood creditor to the extent of several thousands to a company dealing in secondary metals. They had done business together for years. A little while ago the company had not been able to pay its temporary loans with the usual promptness. Additional money was borrowed and things went from bad to worse. The vice president supervising such accounts was about to sell them out for what he could get when a superior officer in the bank thought of a firm of consulting chemists and engineers. He asked them to look over the situation and report the possibilities. A survey of the premises disclosed very little activity in secondary metals but a considerable volume in other recovered values. They found that the sole chemist on the job had been handicapped in his work, that the business began to fall off with the advent of new alloys which they were unable to unscramble, and that the miscellaneous secondary merchandise to be seen everywhere had been taken on in the hope of supporting the six family partners depending on the business. For once a bank took technical advice. The experienced chemist was put in a building elsewhere. He was properly supported in his work and given assistants. The technic was rapidly perfected. The complex alloys in the scrap ceased to give substantial difficulty, and now the loan is being gradually discharged.

There is a great deal of this sort of thing going on. Our banking friends delight in the statement of the certified public accountant, which is a record of what has happened, and from this they try to project what may happen. They have not yet fully realized that it is the chemical audit that can better tell the story of where you are today and what your prospects may be for tomorrow. They have yet to learn that the attitude toward research is a better indication of the endurance and future of a manufacturing company than is its balance sheet.

The banker is very much like the rest of us. We have made him an idol without considering how he came to deserve a halo and now we are disappointed in our own judgment. We realize that much of what we have regarded as capital, as represented by pieces of paper, will have to disappear, if it ever actually existed, before we can really get down to a sound working basis. If the financier and the business manager, recognizing this unpleasant fact, will but make the most of what technology offers, there not only will be ways out of many present difficult situations, but a defense will be created which can withstand any tendency to repeat our bitter experiences.

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MUSCLE SHOALS IN A NEW ROLE. As the years have gone along, even those reluctant to see the facts have been compelled to realize that Muscle Shoals can no longer be characterized as a factor essential in national defense. We even believe that a large number of those who must make the final decision regarding the property know that actually it is important only as a power development, but such a sane consideration appears unacceptable to those who claim to help the American farmer. The last Muscle Shoals Commission has unanimously reached the following conclusions:

> 1. It is economically feasible and desirable to use and operate the Muscle Shoals properties for the following purposes:
>   (a) Primarily for quantitative production of types of commercial fertilizer and/or fertilizer ingredients of greater concentration than those which are now genally sold to the farmer.
>   (b) Coöperative scientific research and experimentation for the betterment of agriculture.
>   (c) Manufacture of chemicals.
>
> 2. It is the definite conclusion of the commission that the foregoing public benefits can best be obtained by private operation under lease contracts through competitive negotiations.

Obviously, the commission has retreated to the last line of trenches—namely, the position that concentrated fertilizer can be produced at Muscle Shoals, either in a form or at a cost not possible with commercial enterprises now operated. It should be noted that the foregoing conclusions of the commission are contrary to the opinion of the chief of the Bureau of Chemistry and Soils and that his views have been endorsed by the Secretary of Agriculture. In the secretary's memorandum of September 29, 1931, addressed to the commission, he repeats the question: "The commission would also appreciate a statement of your general views as to the most practicable use to which the Muscle Shoals project may be put in the interest of agriculture." The answer follows: "An attempt to find a use for the Muscle Shoals project in the interest of agriculture discloses the fact that the objective which it was believed could be accomplished by its operation has already been achieved by other means. Prices of nitrogen fertilizers have been greatly reduced. Ammonium sulfate, the world's leading nitrogen fertilizer, is now quoted at $23 to $26 per ton. Before the World War the average price was $60 per ton and in 1918 and 1920 it sold as high as $150 per ton."

While much has been said and written regarding concentrated fertilizers, there is still a great deficiency of information as to their proper use. Notwithstanding sincere efforts to create a large demand for them, it remains limited. Concentrated fertilizers have not met a ready sale, in spite of well-directed educational and sales campaigns conducted in behalf of such products as Nitro-phoska, Ammo-phos-ko, and Ammo-phos. At any rate, the results in this country have been disappointing, for the sales of Nitro-phoska, which has been well advertised for several years, have not exceeded 12,000 tons per year, as indicated by imports. When it is remembered that the total domestic fertilizer sales approximate 8 million tons per year, it is evident that even this high-grade concentrated fertilizer has enjoyed but a very small demand. Furthermore, several of the larger domestic fertilizer manufacturers have attempted to develop outlets for moderately concentrated fertilizers, but the sales have been small, despite the fact that the agricultural experiment stations and colleges and the National Fertilizer Association have whole-heartedly supported the use of such plant foods. This experience leads to the conclusion that a demand of any size for concentrated fertilizers is non-existent at the present time, even in the territory adjacent to Muscle Shoals.

Our fertilizer industry without doubt could readily increase the concentration of mixed fertilizers as much as 20 to 25 per cent with economy to itself and to the farmer, if there were sufficient demand. There is supplied to the farmer the grade of goods which he requests and which he knows best how to apply. As an indication of this we cite the report of the Commissioner of Agriculture of the State of Mississippi for the year 1930. The state law requires a minimum plant food content of 16 per cent. The report shows that, for the year 1930, 89 per cent of the sales of mixed fertilizers was of the minimum grade and that 95.7 per cent contained 18 per cent or less of plant food.

Another interesting point is that in many sections of the country, more particularly in the large fertilizer-consuming areas of the southeast, it is becoming generally recognized that highly concentrated fertilizers are not as efficient as the well-balanced fertilizers of moderate concentration which have been used in the past with more or less empiricism. The fact is often overlooked that, in order to produce a fertilizer of high concentration, such essential plant foods as calcium and sulfur are generally omitted, whereas the ordinary mixed goods based on superphosphate carry these elements in adequate proportions. In Circular 91 of the Georgia Experiment Station, December, 1930, is a report of yields of seed cotton, using comparable quantities of complete fertilizers but varying the source of phosphorus. Using ordinary 16 per cent superphosphate, the yield of seed cotton in pounds per acre was 668, with diammonium phosphate, a concentrated type, 507 pounds, and with monoammonium phosphate, 549 pounds. The relative yield for the last two named, taking superphosphate as 100, is 76 and 82, respectively. The circular goes on to report that, when limestone was applied with the concentrated phosphate fertilizers, the yields were markedly increased, indicating that two factors—namely, calcium content and soil acidity—are of extreme importance in fertilizer practice. Fortunately, ordinary phosphate available today at bargain prices approaches very closely the ideal phosphate fertilizer. In the effort to cut costs, vital factors of plant nutrition must not be sacrificed.

There has been much loose talk about cheap fertilizers, and as we have frequently pointed out, there has been a persistent effort to have the agriculturist believe that, without subsidy other than that involved in the transfer of the Muscle Shoals property, the plant there could be operated to produce a really cheap fertilizer in a quantity to affect American agriculture generally. At the present time ammonium sulfate, which continues to be the world's leading nitrogen fertilizer, is offered at approximately one-third of the average pre-war price. By-product ammonium sulfate, produced at the coke plants, brings in the neighborhood of $14 or $15 per ton at the point of shipment. These figures show that America is not at a disadvantage and this form of plant food is indeed offered at bargain prices. It is difficult to see by what magic procedure a new group is to enter into a business now characterized by a world overproduction and achieve even a small per cent of the advantages claimed to be possible. We cannot see how a plant can be economically operated on a business basis for the purpose, nor does there exist any emergency or other peculiar set of circumstances which would justify the operation of Muscle Shoals at public expense.

As time has passed, the utter folly of the prior bills and proposals urging the production of fixed nitrogen at Muscle Shoals has been amply proved. The latest recommendations, save for the second conclusion favoring private operation, are equally unsound. Even the commission reports that no acceptable bid has been received from private interests. Notwithstanding the honest efforts of the commission to evolve an acceptable solution, there continues to be too much of politics, too much of tradition, and too little common sense in the Muscle Shoals problem.

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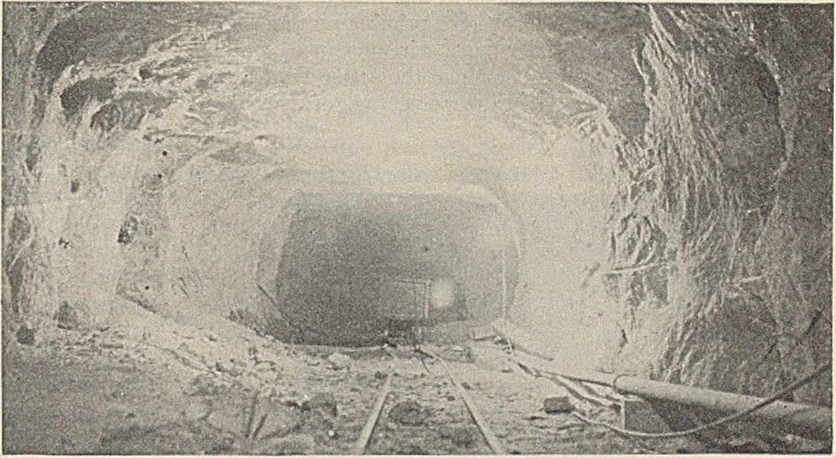
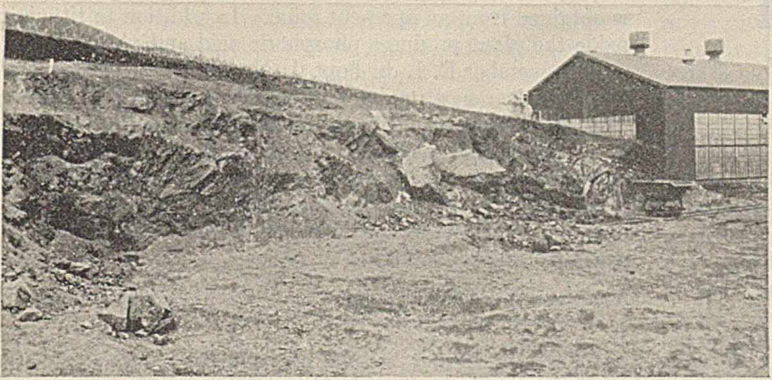
THE AMERICAN CHEMICAL SOCIETY enters upon the new year with confidence that its constructive program will move forward, notwithstanding the difficult times. Our national officers are capable of carrying their responsibilities. Local section officers, in addition to ordinary duties, have unusual opportunities for service in furthering employment. Encouraging news of such activities reaches us from many localities and while new places are slow in developing, specialists are being placed. Lists of our national, divisional, and local section officers appear in each issue of the *Journal of the American Chemical Society*. Learn who these officers are. Support them in their SOCIETY activities.

1931 Passes in Chemical Review



Right: First American Potash Mine. U. S. Potash Co., Loving, N. Mex.



Below: Open-Pit Mining of Nelsonite at Southern Mineral Products Co. Ore milling building in background.

STRIPPED of its many confusing details, the picture of 1931 stands out as a return to stark disagreeable reality after pleasant dreams. Economic standards reached during the past decade which we had all fatuously believed to be permanent, have disappeared, leaving everyone groping for something to replace them. Nothing tangible has yet appeared in their stead, and the unwillingness and inability of everyone to accept the necessity for general revaluation have seriously hindered efforts to achieve stability.

The uncertainty which this has fostered was reflected in the instability of financial institutions and led to the withdrawal of huge sums of money from normal investments and business. Hoarding of cash in this way resulted in serious reduction of employment, as funds for business purposes were practically unobtainable, and this, with other factors, brought on during the early fall what amounted to a banker's panic. This resulted from extraordinary cash withdrawals throughout the country and left the banks generally with so large a proportion of frozen assets as seriously to endanger the country's financial standing.

The formation, at the instance of President Hoover, of the National Credit Corporation to act as a clearing house for liquid capital between banks to save them in case of runs, or threatened runs, accomplished much to restore confidence, and averted, as many believe, consequences of the utmost seriousness for all.

As this is being written, the restoration of confidence is proceeding very slowly; hoarded funds are returning to the banks and to normal investment channels, and there is ground for hope that the period of groping uncertainty may soon be over. It would be unjustifiably optimistic to anticipate that we are going forward to any such period of artificial prosperity as characterized the years preceding 1930, but one may also discount the dismal prophecies of others who see nothing but thick gloom ahead for many years to come.

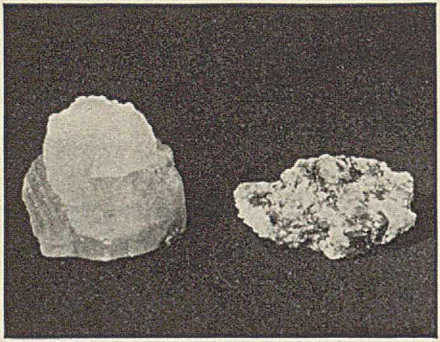
EFFECT OF DEPRESSION UPON CHEMICAL INDUSTRY

Such a discussion as this of economic factors is a strange introduction to a chemical review, but it could not be omitted without detracting from the coherence of the account of events. It is impossible here to detail the contraction of credits, the shrinking of investments, and the growth of fear which have contributed to the economic unrest of the year, but it is equally impossible to understand the effects without at least a sketch of the underlying causes.

In the chemical industry as in all others we find a narrowing of markets and a tightening of the belt in preparation for eventualities. Under the circumstances it is to be expected that fear of the huge expense involved in launching new ventures has minimized the number of these pushed out of development into production during the year, and that despite every good intention many corporations have been forced to reduce their pay rolls. Unemployment has been both a result and a cause of this financial stringency.

Among chemists and chemically trained workers of what might be considered professional standing, the extent of unemployment has been small compared with other groups, presumably because the last decade has firmly implanted the lesson of 1921 in the minds of executives. In 1921 research departments were still considered more or less extraneous to the real business of manufacture and sale of commodities, and consequently were jettisoned at the first indication of a storm. In the period that followed, business battles were won so consistently by the best research organizations that this activity has now been closely integrated into an essential position in corporate structures. At the same time men with research training have risen to posts of responsibility in corporate affairs so that research workers now have friends at court in a way that they did not have before.

Consequently during the present disturbance, research has occupied a preferred position, with insurance and other essentials at the bottom of the list of slashes instead of near the top. While production and even sales forces suffered in 1930, research staffs were held practically intact well into 1931, and even then were pruned with great caution. Although there have been exceptions to this rule, generally the reduction of research forces has been a pruning process rather than a deforestation. Under such circumstances one is gratified to find that the membership of the American Chemical Society shows a relatively low percentage of unemployment.



Specimens of Sylvite Mined at Loving, N. Mex., by U. S. Potash Co.

Whatever statistics one may gather, the fact of unemployment and consequent suffering cannot be wished away. While the *number* of unemployed chemists is not great, the average *period* of idleness for each is far above normal. During normal periods the number of unemployed may be a considerable proportion of the present figure and each of them may anticipate an average period between employments of not more than one or two months, whereas in the present situation the average interval of idleness is increased by the same factors which reduce the number of unemployed, to several times this length of time. In other words, the present effect is multiplied in its consequences by the time factor.

To assist in reëmployment, local sections of the Society are organizing and operating committees made up of the unemployed themselves to assist in the problem of finding and creating openings. The New York and North Jersey Sections, where conditions are worst, are leading in this movement.

Many anomalies have developed as a result of these conditions. It is difficult to reconcile the efforts of employers, particularly in the chemical industry, to adopt a 6-hour working day to allow more men to remain gainfully employed, with the strike of some 35,000 textile workers in New England against a reduction in pay. The 6-hour day, promulgated in the chemical industry by the Manufacturing Chemists Association, has been put satisfactorily into effect by a number of leading chemical companies and has served to stretch pay rolls over a greater number of workers. The striking textile employees after weeks of futile negotiation attempted finally to return to work only to find that demand for their services had materially diminished, and that managements were reluctant to make any sacrifices to reëmploy them.

We have, too, the striking picture of one organization, the Monsanto Chemical Company, raising wages when everyone else was reducing payrolls, or grimly fighting to prevent doing so. This corporation explained its move as a substantial acknowledgment of loyalty which it made for the purposes of raising morale. It is most unfortunate that others did not, or could not, follow this lead.

New Commercial Ventures

Four new ventures launched into commercial reality against the tremendous industrial inertia of 1931 justify special comment. They stand out as clear indications of the courage of their promoters.

The United States Potash Company, a subsidiary of the Pacific Coast Borax Company, put into operation early in the year its mine near Carlsbad, New Mexico. This mine, the only shaft mine operated for potash in America, yields sylvite (potassium chloride) from a depth of 1200 to 1400 feet of sufficient purity for sale as manure salt after simple grinding and without concentration. The output of this mine has been maintained at a rate of several carloads per day since early spring. The deposit being worked is reported to be enormous and apparently is in a similar formation to deposits found farther south in Texas at a greater depth.

The Southern Mineral Products Company, a subsidiary of the Vanadium Corporation of America, began production of titanium oxide pigments and other chemicals at Piney River, Va., in April. This plant operates on ore locally produced and turns out high-grade pigment. The ore, nelsonite, is an aggregate of ilmenite and apatite containing magnetite, and is obtained from an open-cut mine. In addition to titanium oxide the plant produces phosphoric acid and phosphates.

In November E. I. du Pont de Nemours & Company announced their new product, "Duprene," a synthetic rubber. This material is being produced at Deepwater Point, N. J., in commercial quantities. Its present field of usefulness depends upon its resistance to water and hydrocarbon solvents suggesting its utilization in hose, rubber valves, etc., for such liquids. Further applications are to be expected. The synthesis follows this line:

Acetylene $\longrightarrow$ monovinylacetate $\longrightarrow$ chloroprene (2-chloro-1,3-butadiene) $\longrightarrow$ Duprene

The finished product contains chlorine and requires no sulfur for vulcanization. The fundamental work on which this development is based was initiated and conducted by and under the direction of J. A. Nieuwland of the University of Notre Dame. The results were published in the *Journal of the American Chemical Society* for November, 1931, to which the reader is referred for a full account of the chemistry of the process.

In connection with this development, it is interesting to note that a small piece of synthetic rubber, believed to be the first ever to be made from petroleum as a raw material, was exhibited in the booth of the American Chemical Society at the 1931 Chemical Exposition. The sample was prepared by B. T. Brooks and was, chemically, rubber. Duprene is a rubber-like synthetic rather than synthetic rubber.

The fourth commercial development of special interest was the beginning of operations by the Standard Chromates Company at Painesville, Ohio, manufacturers of sodium dichromate.

Patents

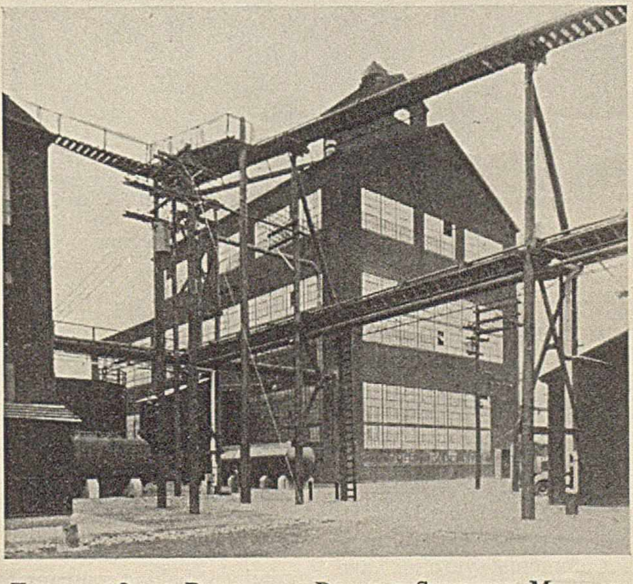
In the field of patents two developments are of special importance, since they are designed to avoid the enormous expense of litigation over patent rights. An agreement was finally reached between the major contestants in the battle royal of the oil-cracking patents, which, it is to be hoped, will relieve this industry of much of the past burden of patent suits, and the parties interested in developing the newer synthetic resins have gotten together without serious litigation in order to avoid it in the future.

Early in the year the Dubbs process was sold to the United Gasoline Corporation, formed for the purpose by the Shell Universal Oil Company, the Standard Oil Company of

California, and the Universal Oil Products Company. The Standard Oil Company of Indiana, the Standard Oil Company of New Jersey, the Standard Oil Development Company, the Texas Company, and the Gasoline Products Company entered into an agreement with the United Gasoline Company to avoid litigation in the future on oil-cracking patents. Later the Gulf Refining Company and the Atlantic Refining Company joined as signatories to the same agreement. This followed the long litigation extending over a period of several years between the Dubbs interest and other holders of cracking patents. Just before the agreement was reached, the Universal Oil Products Company, owners of the Dubbs process, had won an important decision in a suit brought against The Warner-Quinlan Company, a licensee of Universal, by the Texas Company, a fact of some weight in forcing the agreement. The situation in the petroleum industry, as a result of this agreement, is particularly favorable to further developments and progress. Although the royalty agreements made involve a considerable sum of money, it is highly probable that this will be materially less than the cost of litigation. At the present time there are approximately two thousand cracking units in the United States, producing nearly two million barrels daily.

A similar situation of long and expensive litigation is believed to have been avoided in the rapidly developing field of synthetic resins of the phthalate and polybasic types by an agreement between the General Electric Company, the E. I. du Pont de Nemours & Company, the American Cyanamid Company, and the Ellis-Foster Company. This agreement, in effect, binds the parties to reciprocal respect of one another's patents and applications bearing on this subject. The objective was to avoid hampering the developments of these useful resins by legal complications. The resins in question are known as the glyptal, alkyd, and rezyl resins. The contract on which agreement was reached is too long, too involved, and too private to permit review here.

In maintaining the reputation acquired during recent years, the Supreme Court of the United States has invalidated two patents, among others, of rather important industries during the year. United States Patent 1,529,461, covering the treatment of fruit with borax to prevent mold during transit, was declared invalid on the grounds of prior disclosure. The method outlined in the patent consists of the treatment of fruit, particularly citrus fruit, with a dilute solution of borax, leaving a thin film of this material on the skin of the fruit to prevent the growth of molds, particularly blue mold, which take an enormous annual toll from citrus fruit shipments.



Titanium Oxide Building in Plant of Southern Mineral Products Co., Piney River, Va.

One of the patents upon which the DryIce Corporation of America based its claim to a monopoly in the manufacture and use of solid carbon dioxide for refrigerating purposes reached the United States Supreme Court during the year without disagreement between circuits, and in a somewhat involved proceeding was declared invalid. The patent in question covered the combination of an insulated container, a perishable product, and solid carbon dioxide in a particular manner to achieve unexpectedly high calorific efficiencies in the use of this refrigerant. The elements of the combination were admitted to be unpatented and unpatentable. The DryIce Corporation of America had brought suit against the Carbice Corporation, basing its suit on the sale by the defendant of solid carbon dioxide intended to be used in making the patented combination. This suit reached the Supreme Court, and its decision rendered in February of this year was to the effect that such a patent on a combination of unpatented elements could not be used to control the unpatented elements. Later a rehearing before the Supreme Court was had on the same patent on a technicality and it was declared invalid. This decision had been largely discounted by others interested in solid carbon dioxide, and 1931 saw a number of companies mature plans and actively launch into the manufacture of the material.

The validity of the patents upon which the du Pont Company has endeavored to maintain a monopoly on low-viscosity cotton for lacquer use has come into serious question during the year, and a group has been formed, designated as the Lacquer Trustees, to assist independent companies in fighting suits brought against them on the basis of the du Pont patents. In effect, this amounts to a war chest upon which any contributor attacked may draw to assist in his defense. Already the fund has been so used.

It is of special interest to note that the first patents on plants were granted in 1931. Provision was made by law in 1930 for patents on asexually produced plant varieties, and so far five patents of this kind have been issued. In order to make the subject matter clear, two of these are illustrated in color, a new departure in Patent Office practice.

PURE CHEMISTRY

In pure chemistry the completion of the periodic system of ninety-two elements is probably the most significant development. In 1930 Allison, Murphy, and their coworkers at the Alabama Polytechnic Institute announced the discovery of eka-cesium, atomic number 87, by the use of a magneto-optical method. The method, based upon the long-known effect of a magnetic field on polarized light, is new, and the results obtained have not been checked by others. In the meantime Jacob Papish at Cornell University, using more orthodox methods, announced in 1931 the discovery of element 87 in samarskite. A controversy has already started on the priority of discovery. The Alabama Polytechnic group has also announced during 1931 the discovery of eka-iodine, atomic number 85, in a number of halogen-bearing materials. Whatever may be the ultimate award of credit to, or between these investigators, there is in the situation much to stir the imagination of a mere chemist. First, one is struck by the accuracy of Mendeleeff's theory, propounded sixty years ago. Although subjected to the most searching investigation during chemistry's most prolific period, his generalization on periodicity of properties of the elements has stood the test of time, and with relatively slight modifications has received only the strongest confirmation in an era of refinement of observation beyond the wildest dreams of Mendeleeff's day. One may take pardonable pride in a professional kinship with a mind so powerful, and one also finds inescapable the thought that great minds vault over inadequacies of human limitations with an apparent ease that makes intricate equipment seem unnecessarily burdensome.

The future, too, must engage one's thought. Is it conceivable that only 92 elements comprise the entire universe? That no more remain to be found? Perhaps that is the situation, but the inquiring mind refuses easily to accept it. The theory of Sir James Jeans, eminent British astrophysicist, offers solace to those who would weep for other elements to find by suggesting that within the fixed stars there may be elements, whole periods of them, of atomic weights far greater than that of uranium. This theory attains plausibility by suggesting that the gaseous envelopes of these enormously hot bodies mask heavy atoms by reducing their emitted radiation below the level at which we can detect it. In other words, it proposes a serious problem in refinement of apparatus to allow us to continue the search and holds out the possibilities of whole periods of unknown elements. Certainly the addition of a single new element to the list now immediately calls for the discovery of enough to complete a new period.

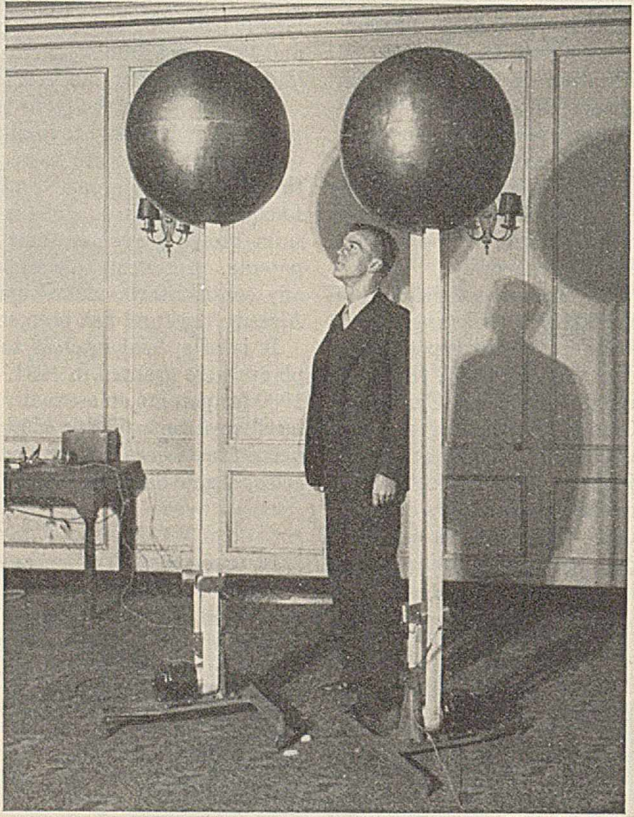


Photo by Acme

Van de Graaff High Voltage Generator

The first sample of the element, rhenium (atomic number 75 and discovered in 1925), was exhibited at the Chemical Exposition in New York in May. It is a source of considerable satisfaction to those of us who still rely on our own senses rather than upon x-rays and modern physical concepts to be able to see and feel actual specimens of newly discovered elements.

In Europe the problem of depoisoning illuminating gas by the elimination of its carbon monoxide content is receiving more serious consideration than on this side of the Atlantic. Refrigeration methods employed in separating carbon monoxide from nitrogen to be used for ammonia synthesis have been proposed for commercial gas purification, but the latest suggestion comes from Franz Fischer, of Berlin, who has demonstrated the ability of bacteria to convert a carbon monoxide-hydrogen mixture into methane. Whether this will ever become a commercial fact remains to be seen. Certainly it presents interesting possibilities.

In the field of photochemistry new demands urgently made by talking motion pictures have been met by vast strides ahead in the science and art of photography. Increased speed of film allows the noisy Klieg lights of the old days to be replaced by silent incandescents giving a soundless light far less objectionable to those exposed to it, and a new film sensitive to infra-red rays now allows photographs to be taken in the dark.

Among the interesting confirmations of physical-chemical theory has been the proof adduced by the medical profession of the theory that coagulation of the protein of the brain is closely bound up with insanity. Wilder D. Bancroft of Cornell has maintained that from a physical-chemical point of view insanity is caused by either a coagulation or a dispersion of the brain proteins. It has been shown clinically that, in certain instances where the brain proteins were coagulated, the administration of sodium thiocyanate disperses the coagulum and cures the disorder. Coagulative treatments have been shown to be beneficial where the insanity is of a disperse type. Bancroft's further theory states that an anesthetization involves coagulation of the brain and nerve tissue.

Continually research is developing the fact that metals, even in minute quantities, are essential to normal life. During the year McCollum and Orent, at Johns Hopkins University, have determined that magnesium is essential to the normal diet. About the tenth day on a diet free from magnesium, experimental rats went into spasms, and most of them died. The presence of magnesium in the diet is necessary, according to these investigators, to the proper functioning of the adrenal glands.

An element essential in life has been discovered, but not identified, among the proteins of milk by W. C. Rose and his co-workers at the University of Illinois. Synthetic diets containing all the twenty known amino acids stunted the growth of white rats. The addition of milk casein made the rats grow normally. A potent fraction of the milk casein has been prepared and its effectiveness proved.

Investigators at the Toronto Hospital for Sick Children have prepared white bread containing appreciable amounts of vitamins B, D, and E without changing the appearance or taste of the bread and at no advance in cost to the consumer. This recalls the unsuccessful effort made some years ago by a prominent baking company to market a white loaf containing all the essentials of a complete diet.

A recent news dispatch from Germany reports that vitamin D has been isolated from irradiated ergosterol by Adolf Windhaus of Berlin. While infinitesimal dosages cure rickets, the report says, a quantity of 50 milligrams is dangerously large.

Ottar Rygh at the University of Upsala, Sweden, succeeded late in the year in crystallizing pure vitamin C.

Commercial application of the use of filtered radiation for purposes of sterilization and creation of vitamin D are proceeding in the hands of the General Foods Corporation on the basis of researches carried out under the direction of George Sperti at the University of Cincinnati.

In the affairs of the AMERICAN CHEMICAL SOCIETY several items are important as matters of record. In spite of the widespread effect of the economic depression, the fall meeting of the SOCIETY at Buffalo had a registration of 2057, which is next to the largest registration at any meeting the SOCIETY has held—the largest having been that at the Sesquicentennial Exposition at Philadelphia in the fall of 1926 with a total registration of 2249. The directorate of the SOCIETY was enlarged to fourteen members. Few realize that the illustrious Thomas A. Edison, who died in October just before success was achieved in his last project to make rubber from golden rod, was a member of the AMERICAN CHEMICAL SOCIETY for twenty-three years.

Two new awards in American chemistry were made in 1931. The AMERICAN CHEMICAL SOCIETY award, made possible through the generosity of A. C. Langmuir, was given to Linus Pauling, of the California Institute of Technology, in recognition of his fundamental work in physical chemistry. The Jacob F. Schoellkopf medal of the Western New York Section, A. C. S., was awarded Frank J. Tone, of the Carborundum Company for outstanding industrial achievements.

PHYSICS

The American Institute of Physics, with Karl T. Compton, president of Massachusetts Institute of Technology, as chairman of its governing board, was formed during 1931 through the coöperation of the American Physical Society, the Optical Society of America, the Acoustical Society, and the Society of Rheology. One of the objectives of the newly-formed Institute is to secure the publication of research results in physics and abstracts of printed work in physics published throughout the world. The Chemical Foundation, Inc., has undertaken to handle the business end of the Institute's publication program.

Robert J. van de Graaff demonstrated at a dinner of the American Institute of Physics, held in New York, an electrical machine for accumulating a charge of 1,500,000 volts, and capable of enlargement to produce 50,000,000 volts. Although materially modified for the present purpose, this machine operates on the same principle as that of the original static electric machines, two large metal spheres being used to accumulate charges at high potentials. With it van de Graaff expects to be able to disintegrate atoms in the course of research now being initiated at Massachusetts Institute of Technology.

R. A. Milliken, Nobel prize winner in physics, announced during the year a multiple crystal spectrometer for use with x-rays developed by Dumond and Kirkpatrick at the California Institute of Technology, with which it is possible to photograph and measure the velocity of electrons. Milliken stated that this machine, which consists of fifty quartz spectrographs arranged in series, gives the first evidences of a dynamic, as opposed to a static atom.

MISCELLANEOUS

H. C. Urey and G. M. Murphy of Columbia University and F. S. Brickwedde of the Bureau of Standards announced the separation of hydrogen into its isotopes.

Radium deposits were discovered at Echo Bay on Great Bear Lake, 1200 miles north of Edmonton, Alberta County, Canada.

A new honorary fraternity in chemistry, Theta Chi Epsilon, was founded during the year at the University of Illinois.

Radium introduced into food and drink is said greatly to prolong life, making another worry to be added to our accumulated store if we expect to live as long as our ancestors. Dr. Gable of the Detroit Institute of Technology has reported that he regularly drinks radium high-balls, consisting of fruit juices through which a small quantity of radon has been forced, and he reports that this has helped him keep in fine physical condition. It is, however, not recommended that radium high-balls be drunk generally without specific control and advice.

Intricacies of the prohibition laws have finally persuaded the government-subsidized wine-grape industry of California to modify its marketing policy of supplying grape juice to the consumer and supervising its conversion into wine in the home. The Vine Glo Corporation, marketing subsidiary of Fruit Industries, Ltd., states that its grape-juice product will now be marketed solely for use in soft-drink preparations. It will be recalled that the Federal Farm Board recently loaned Fruit Industries $3,500,000 to assist it in marketing California's grape surplus, and that the marketing corporation has carefully supervised the grape juice through the fermentation process in the home of the consumer. Now apparently responsibility will no longer be shared by the corporation but must rest entirely on the consumer himself.

Lyell M. Rader, who achieved fame shortly after the war by finding the key to modern chemistry in the Bible, was again in difficulties during 1931. Norman Rosie, of whom nothing more is reported, sued Rader to recover a sum of $30,500 advanced to the latter to assist in the promotion of a cracking process for manufacturing gasoline from crude oil. It will be recalled that Rader was similarly sued in 1925 for the return of a sum of money advanced on his claim to a secret process for the manufacture of carbon black from Arkansas lignite. Rader's activities, which have consisted of alternate chemical and evangelical campaigns, have brought him frequently into prominence both as a religionist and as an alleged inventor. Rader was responsible, according to his own account, for the discovery of a method of purifying T. N. T. by the use of water melted from the snow obtained from the top of the Alps Mountains, which process, he claimed, was of enormous value to the Allies in winning the World War.

It should also be recalled that John F. Veale, one of the group headed by "Doctor" Walter von Hohenau, was arrested in November and charged with unlawfully using the United States mails in furtherance of a scheme to defraud. Hohenau was the alleged genius who proposed to manufacture hydrogen by completely breaking down water to this single element, using the electric current derived from an ordinary house-lighting socket. This adventure was given wide publicity through the NEWS EDITION some years past; and about two years ago Hohenau, then operating in Germany, was arrested on a charge of murder. The police, according to the report, had been suspicious of Hohenau, largely because of his American activities, and had placed a guard in the laboratory where he was supposed to be making inventions. It is stated that the guard was killed in a quarrel, and Hohenau escaped, only to be captured later. Veale is closely identified with the Hydro-Production Corporation of Delaware and the famous International Chemicals, Inc. The charges of unlawfully using the mails were based upon letters written in connection with stock sales and the operation of the two companies. Unfortunately some $200,000 worth of stock in these enterprises was disposed of in Delaware and vicinity, notwithstanding the sustained efforts of local business men and scientists to prevent the mulcting of the citizens of their community.

The record of the sciences in the year just past is encouraging, and with the opportunity afforded for the completion of research projects and the initiation of new investigations there is needed only a tendency toward normal business to bring prominently into view during 1932 a number of new improvements.

Symposium on Utilization of Gaseous Hydrocarbons

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.

GASEOUS hydrocarbons present an excellent potential source of raw material for chemical manufacture. Everyone is cognizant of this fact but few appreciate why this potential source does not become a real source.

At least two important reasons can be given for this failure to utilize our gaseous hydrocarbons. First, most chemical reactions involving gaseous hydrocarbons take place with an evolution of heat. It is difficult to obtain the necessary heat transfer in order to maintain proper temperature conditions. Proper temperature conditions or the confining of the reaction temperature within narrow limits are absolutely necessary in order to produce the pure products desired, instead of a complex mixture.

A second reason is evident when we consider that even though there is no great evolution of heat in certain reactions involving gaseous hydrocarbons, nevertheless there is great difficulty in operating these reactions under what might be considered reasonable equilibrium conditions. This is probably due to the fact that reasonable equilibrium conditions necessitate reactions at very high temperatures and high pressures. Satisfactory equipment to meet such conditions has only recently been developed.

Lately there has been an attempt on the part of investigators in this general field to utilize pure organic compounds rather than mixtures. This is apparently a step in the right direction as shown by the increase of interesting results obtained in this field.

It is believed that the papers in this symposium will clearly substantiate the statements made above.

One peculiar economic feature of the general problem should be noted. The present large use for hydrocarbons is as motor fuel; approximately 20 billion gallons are produced per year in this country. The next largest use for these hydrocarbons that has been proposed is in the production of solvents with only 200 million gallons per year possible consumption. Between the two uses there should be developed a third field before the oil refineries can afford to spend the large sums necessary to utilize the hydrocarbon gases. Two possibilities have recently appeared. One is the use of hydrocarbons in the manufacture of synthetic resins to be used in paints, varnishes, lacquers, and plastics. The other is the use of hydrocarbon gases in the manufacture of new synthetic textiles—for example, the polymers of glycol sebacate.

D. B. KEYES, *Chairman*

Partial Oxidation of Hydrocarbons Catalyzed by Oxides of Nitrogen

C. H. BIBB, *Oxidation Products Company, Jersey City, N. J.*

THE OXIDATION of methane to formaldehyde and methanol has been involved in most of the work of the past. However, considerable quantities of formaldehyde can be obtained from propane and other hydrocarbons by the process, and, as has been described, phenol is the principal oxidation product when benzene is used. In this article, operative conditions of a few runs are described which show better yields on the hydrocarbons and oxides of nitrogen to formaldehyde than have heretofore been published.

THE use of the oxides of nitrogen to catalyze the partial oxidation of hydrocarbons with air has principally been described in articles by Layng and Soukup (*3*), Smith and Milner (*4*), and Bibb and Lucas (*2*); and in patents to the author (*1*). The process consists essentially in mixing air and a gaseous hydrocarbon together with a relatively small amount of oxides of nitrogen, heating the mixture to a reaction temperature which may vary between 500° and 900° C., cooling the mixture, and condensing out the aqueous solution formed from the fixed gases. The fixed or exit gases may be processed again for additional oxidation products by mixing with more air, with or without the further addition of nitrogen oxides, or they may be recycled in the original heating chamber. The proportions of hydrocarbon, air, and nitrogen oxides; temperature; velocity of the gases through the reaction zone, or the time of heating; form of reaction chamber; and the nature of the hydrocarbon all have pronounced effects on the results obtained.

OXIDATION OF NATURAL GAS

In addition to the simplest method of partially oxidizing the hydrocarbons of natural gas, which consists in only a single pass of the gaseous mixture through the reaction zone and the condensation of the oxidation products, the tail gases were oxidized successively four times. In another series of experiments the recycle principle was used whereby the tail gases from the condensation apparatus were conveyed back to the inlet of the reaction zone and reoxidized. In some experiments the recycle rate was over fifteen times the amount of input into the system. A bleed-off of the gases was, of course, necessary in order to maintain constant pressure.

SINGLE-PASS TREATMENT

Using the first unit of a four-pass system as an illustration of a single pass, the apparatus set-up was as follows: An air blower supplied air under slight pressure which was conducted through a drying chamber filled with anhydrous calcium chloride and then through an orifice meter to measure the rate of flow. From the meter the air was bubbled through 66 per cent nitric acid contained in a flask immersed in a constant-temperature water bath, the temperature of the bath determining the amount of acid picked up by the air. From the acid flask the air was lead to a tee where it was mixed with metered natural gas delivered from a gasometer. The gaseous mixture was then passed through the reaction zone, which consisted of a chrome-nickel steel tube of 2.2 cm. inside diameter, heated for 25 cm. of length in an electric furnace with automatic temperature control. The gases from the reaction zone were immediately conducted to a 60-cm. aluminum condenser where an aqueous solution of formaldehyde and methanol collected. The gases were finally scrubbed in a glass tower filled with beads, down the inside of which water was allowed to trickle, the gases going in at the bottom and out at the top. The formaldehyde in both condensate and tower washings was analyzed by the hydrogen peroxide method. The natural gas used had the following composition, in per cent by volume:

Methane	80.40
Ethane	16.55
Illuminants	0.60
Carbon dioxide	0.10
Oxygen	0.45
Nitrogen	1.90

The amount of nitric acid consumed was found by weighing the acid flask before and after the experiment, making correction for any change in the acid concentration due to the passage of the air. Thermal decomposition of the acid traveling through the reaction zone formed the oxides of nitrogen which catalyzed the partial oxidation of the hydrocarbons. In some of the runs silica tubes were used instead of the chrome-nickel steel ones. No differences in catalysis were noted, but the rate of heat transfer was greater with the latter. It has been found that, in operating a reaction tube of chrome-nickel steel on a large scale for manufacturing oxidized oil at temperatures above 600° C., such alloys do not materially change after operation of more than 7000 hours. For the purpose of computing yields of the process at 760 mm. pressure and 0° C. temperature, thermometers and pressure gages were placed in the gas and air meters, and the room temperature and barometric pressure were taken during each run. Thirty-one hundred cubic centimeters of natural gas and 7250 cc. of air per minute were passed through this apparatus, the air bubbling through 66 per cent nitric acid at 22° C. just before it mixed with the natural gas. The temperature of the furnace or the outside of the reaction tube was held at 735° C. during the run, which was continued for 2 hours. Forty-eight cubic centimeters of condensate (specific gravity 1.052 at 15° C., and containing 16.83 per cent formaldehyde) were collected from the condenser, and 228 cc. of a weak formaldehyde solution, testing 1.005 specific gravity and 3.0 per cent formaldehyde, were taken from the tower washer. The amount of 66 per cent acid used was 13.5 grams, and the total gas used was 372 liters. The total formaldehyde produced was 15.37 grams. This is equivalent to 41.3 grams of formaldehyde per 1000 liters, or 6.42 pounds of 40 per cent formaldehyde per 1000 cubic feet of natural gas. The ratio of nitrogen dioxide to formaldehyde by weight is 1:2.36, or 1 pound of nitrogen dioxide to 5.9 pounds of 40 per cent formaldehyde.

FOUR-PASS TREATMENT

In the run just described, three more furnaces and reaction tubes were attached to the apparatus with a condenser and scrubber for each furnace so that, after each time the gaseous mixture was passed through a reaction zone, it was cooled by the condenser and scrubbed with water. Thus, four condensates and four tower washings were obtained. At the inlet of each of the three additional reaction tubes, an air connection was made, and air, metered and charged with the vapors of nitric acid, was forced into the main gas stream, thus supplying the last three reaction zones with auxiliary air and nitrogen dioxide. One constant-temperature water bath held all four acid flasks. The last three reaction tubes were of silica (2 cm. diameter) and were heated for 45 cm. of length in automatically controlled electric furnaces.

The data of a 2-hour run with the four reaction zones in series are shown in Table I, and the condensates in Table II.

TABLE I. RESULTS OF 2-HOUR RUN

Natural-gas flow, cc./min.	3100
Air flow No. 1 unit, cc./min.	7250
Air flow No. 2 unit, cc./min.	3550
Air flow No. 3 unit, cc./min.	3550
Air flow No. 4 unit, cc./min.	3550
Temp. of all furnaces, ° C.	735
Temp. of acid bath, ° C.	22
Total natural gas used, liters	372
Total air used, liters	2148
Total 66% nitric acid used, grams	32.0

TABLE II. CONDENSATE DATA

UNIT	VOL. CONDENSATE	SP. GR.[a]	CH_2O	
	Cc.		%	*Grams*
1	48	1.052	16.83	8.49
2	94	1.019	7.25	6.94
3	67.5	1.030	8.74	6.07
4	62.5	1.023	7.80	4.98

[a] At 15° C.

Tower washings (1265 cc.) which were collected from the four washing towers had a specific gravity of 1.003 and tested 1.53 per cent, giving 19.41 grams of formaldehyde.

Thus a total of 45.89 grams of formaldehyde were obtained. This is equal to 123.3 grams of formaldehyde per 1000 liters, or 19.1 pounds of 40 per cent formaldehyde per 1000 cubic feet of natural gas. The ratio by weight of nitrogen dioxide to formaldehyde is therefore 1:2.97, or 1 pound of nitrogen dioxide gives 7.42 pounds of 40 per cent formaldehyde.

EXPERIMENT WITH PROPANE

A run was made on the first unit of the apparatus described, using a gas containing about 90 per cent propane instead of natural gas; results are shown in Table III.

TABLE III. RESULTS WITH PROPANE

Time of run, hours	2
Rate of gas flow, cc./min.	1700
Rate of air flow, cc./min.	8500
Temp. of acid bath, ° C.	25
Temp. of furnace, ° C.	770
Total propane used, liters	204
Total acid used, grams	11.2
Vol. of condensate, cc.	96.5
Sp. gr. of condensate at 15° C.	1.043
CH_2O in condensate, %	15.4
Vol. of tower wash, cc.	1105
CH_2O in tower wash, %	0.96
Total formaldehyde produced, grams	26.1

From these data it is found that 127.9 grams of formaldehyde are produced per 1000 liters of propane for just a single pass through the reaction zone. This is equal to 19.8 pounds of 40 per cent formaldehyde per 1000 cubic feet. The weight of nitrogen dioxide to formaldehyde here is 1:4.83, or 1 pound of nitrogen dioxide gives 12.07 pounds of 40 per cent formaldehyde.

RECYCLE SYSTEM WITH NATURAL GAS

For this work a larger apparatus was made.

A chrome-nickel steel tube of 3.75 cm. inside diameter was used for the reaction chamber; it was heated for a length of 60 cm. The outlet end was connected to a condenser made of aluminum tubing. An aluminum tube of 6.5 cm. inside diameter and 240 cm. length was used for a washing tower. It was filled with aluminum rings, 1 cm. by 1 cm., and connected to a receiver located at the bottom of the condenser so that the gases could pass through the reaction tube, into the top of the condenser and out of the bottom, into the bottom of the washing tower and out of the top. The outlet of the tower was arranged with a bleed-off to the atmosphere. The top of the tower was connected to the recycle pump, the outlet of which was connected to the inlet of the reaction tube, so that the gases could be circulated from the reaction zone through the condenser and washing tower and back to the reaction tube again. The inlet of the reaction tube was also connected to an acid flask for admitting air and nitric acid vapor into the system. The natural gas and auxiliary air were put into the system at the inlet of the recycle pump, since the pressure at this point was below atmospheric pressure. By regulation of a valve on the recycle pump, various rates of flow of gases could be made to circulate through the apparatus. The bleed-off at the top of the tower discharged gases to the atmosphere at a rate about equal to the total input of air and gas. The purpose of the auxiliary air feed was to be able to adjust properly the quantity of air passing through the acid flask, thereby controlling the amount of acid vapor to the system. An integrating meter was placed in the natural-gas line in order to check the total consumption of gas as computed from the reading on the flowmeter. A detailed record of a run is shown in Table IV.

By using less gas than in the above experiment, a yield as high as 50 pounds of 40 per cent formaldehyde per 1000 cubic feet of gas has been realized, or as much 40 per cent formaldehyde as the original weight of natural gas.

COMMERCIAL ASPECTS

The question as to whether the single-pass method or the recycle method would be used commercially depends to a large extent upon the cost of the natural gas; with the single pass, 6 to 7 pounds of 40 per cent formaldehyde could be expected from 1000 feet of natural gas, with the exit gases having a very high B. t. u. content. Using the recycle principle, 30 to 40 pounds of 40 per cent formaldehyde could be reasonably expected, with the exit gases being quite dilute but still burnable as fuel. In the latter case, however, it must be realized that plant capacity for a reaction zone of given size is materially less than in the single-pass method, and from a practical viewpoint it is a question of balancing investment charges with raw-material costs.

Natural gas can be obtained in some localities as low as 3 cents per 1000 cubic feet. Nitrogen oxides from the oxidation of ammonia can be manufactured for 3 cents per pound. The arc method for producing nitrogen oxides can also be applied to the air going into the process, and sufficient concentration of nitrogen oxides obtained to properly catalyze the oxidation. Using a 3-cent gas and assuming single-pass operation with 6-pound yield per 1000 feet, the gas cost would be 0.5 cent per pound of 40 per cent formaldehyde obtained. Using likewise a 3-cent cost per pound of NO_2 and taking a ratio of 1 to 9, which ratio can undoubtedly be obtained in a commercial outfit, would give a catalyst cost of 0.333 cent per pound of formaldehyde produced, or a total raw-material cost of 0.833 cent per pound. Using 30-cent gas and the recycle principle, and assuming a yield of 30 pounds per 1000 feet of gas, the total cost of raw materials would be 1.33 cents per pound. It might be noted that with this process sufficient methanol is formed in the reaction to stabilize the formaldehyde produced.

TABLE IV. RESULTS WITH NATURAL GAS

Duration of run, hours	2.5
Rate of flow of natural gas (uncor.) cc./min.	3560
Rate of flow of air, liters/min.	20
Rate of flow of recycle gases, liters/min.	144
Temp. of reaction tube outside,[a] ° C.	893
Temp. of reaction tube inside,[a] ° C.	790
Temp. of acid bath, ° C.	38
Temp. of room, ° C.	20
Barometer, inches	30.2
Pressure of gas in meter, inches H_2O	2
Temp. of gas in meter, ° C.	16
Total gas used (cor.), liters	508.3
Sp. gr. of nitric acid at start	1.406
Sp. gr. of nitric acid at stop	1.405
Total acid used, grams	55.1
Rate of bleed-off, liters/min.	22
Highest pressure in system, inches Hg	2.37
Vol. of condensate, cc.	264.6
Sp. gr. of condensate at 15° C.	1.048
Formaldehyde in condensate, %	14.33
Weight of formaldehyde, grams	39.74
Vol. tower wash, cc.	3735
Sp. gr. of tower wash at 15° C.	1.003
Formaldehyde, %	1.247
Weight of formaldehyde, grams	46.71
Total formaldehyde produced, grams	86.45
40% formaldehyde produced, grams	216.13
Formaldehyde per 1000 liters gas, grams	170.2
40% formaldehyde per 1000 cu. ft. gas, pounds	26.49
Weight ratio of NO_2 to CH_2O	1:3.23

[a] 20 cm. from exit end.

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(3) Layng and Soukup, *Ibid.*, 20, 1052 (1928).
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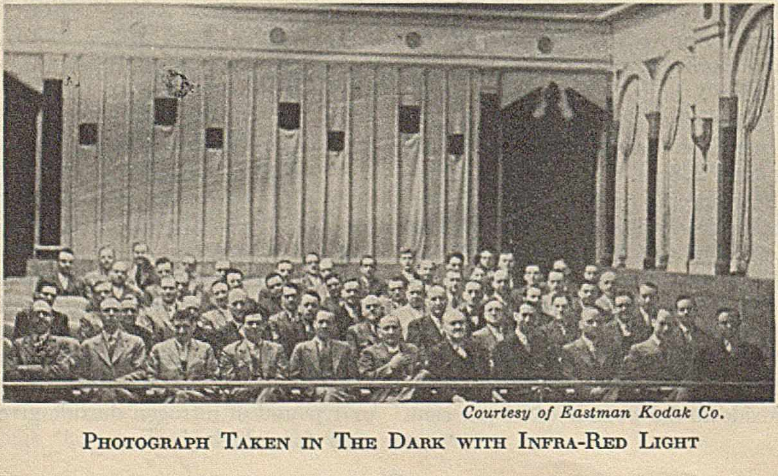
RECEIVED October 31, 1931.



Courtesy of Eastman Kodak Co.

PHOTOGRAPH TAKEN IN THE DARK WITH INFRA-RED LIGHT

This photograph (see text, page 8) was taken in total darkness in the projection room of the new research laboratory of the Eastman Kodak Company on the occasion of the visit of a group under the auspices of the National Research Council.

The source of infra-red radiation was a battery of fifteen 1-kilowatt lamps used in a booth, the top of which was covered with Wratten 87 filter. This filter transmits no visible light but does transmit very freely in the region between 800 and 900 mμ. The plate used had a very high sensitivity to light in this range and was hypersensitized with ammonia. The exposure was one second at f/2.5.

Chemical Utilization of Natural and Refinery Gases

Per K. Frolich and Peter J. Wiezevich, *Standard Oil Development Co., Elizabeth, N. J.*

THE AVAILABILITY and cost of natural and refinery gases are discussed. The reactions of saturated and unsaturated hydrocarbons with respect to cracking, oxidation, halogenation, addition, and polymerization are dealt with in the light of recent data. With respect to relative reactivity of the saturated hydrocarbons, methane is much more resistant than any of the others, as far as chemical changes are concerned, so that violent treatment must be resorted to in order to convert it into more desirable products.

This survey of possible methods for the utilization of gaseous hydrocarbons has shown that, with such raw materials, it is possible to prepare a wide variety of aliphatic, aromatic, and naphthenic compounds. Of these, the olefins appear to offer the greatest possibilities for utilization in chemical processes. These unsaturates are readily available in refinery gases and may be obtained in practically unlimited quantities by cracking of the natural-gas hydrocarbons. There are at present a number of processes in operation for the manufacture of derivatives of olefins obtained from both sources, the products being used chiefly for solvent purposes. Expansion in these industries will undoubtedly take place as the market for their products increases, and new processes will surely be developed. However, the limitations in the knowledge of the organic chemistry of the lower aliphatics and the practically complete lack of physical data on their derivatives, will for some time to come continue to handicap progress in this field.

THE aliphatic hydrocarbons of low molecular weight available in this country in abundant quantities and at low cost as natural gas, and to a more limited extent as refinery gases, are continuing to attract the attention of the research chemist as potential raw materials for the manufacture of a variety of chemical products. The total amount of natural gas available daily in the United States has been roughly estimated at 53 billion cubic feet. Its composition varies considerably, ranging from nearly pure methane to mixtures containing upward of 50 per cent ethane, propane, and higher hydrocarbons in gradually decreasing amounts. Refinery gases, produced in much smaller quantities than natural gas, contain hydrogen and unsaturates in addition to saturated hydrocarbons. The amounts of unsaturates present vary according to the feed stock and also according to cracking conditions, being greatest in gases obtained by cracking oils at high temperature and low pressure. Varying amounts of hydrogen sulfide and other sulfur compounds may also be present, depending upon the source of the material.

At present these gaseous hydrocarbons are chiefly used as fuel. Compared with 13,000 B. t. u. coal at $4.50 per ton, they have a fuel value of 17.3 cents per million B. t. u., corresponding to 17.2 cents per thousand cubic feet of methane. On the same basis, propane would be worth 42.6 cents per thousand cubic feet. (This figure refers only to the calorific value of the hydrocarbon and does not include charges incidental to its recovery in the pure state from mixed gases.) Although such a direct comparison with coal is not entirely justified, since a gaseous fuel frequently demands a premium, there are many cases where even these prices are too high. For example, in some of the Texas and California oil fields producers are looking for disposal of their natural gas at a cost sufficient to pay for the piping and distribution, which, over local areas, usually amounts to about 3 to 5 cents per thousand cubic feet. In many instances there are no outlets whatever, and consequently the gas is disposed of by burning in the open air. However, in considering the gas as a raw material for chemical processes, it must be borne in mind that high freight rates and other factors in such remote localities tend to offset the advantage of the lower raw-material cost.

Naturally the oil industry is concerned with finding suitable new outlets for these materials, but, so far, only little progress has resulted in this direction, in spite of the efforts made to convert them into more useful and valuable products. The paraffins usually included in the term "gaseous hydrocarbons" are methane (boiling point, −259° F., −161.4° C.); ethane (boiling point, −127° F., −88.3° C.); and propane (boiling point, −44.0° F., −42.2° C.). The pentanes (boiling point from 28.0° to 36.1° C., or 82.4° to 97.0° F.) are liquid at room temperature, and constitute an important part of the light ends in motor fuel. The butanes (isobutane, boiling point, −12.2° C., 10.0° F., and *n*-butane, boiling point, −0.6° C., 30.9° F.) are on the border line, in that there is a limit to the amounts which can be safely incorporated in gasoline. The corresponding olefins have boiling points so close to the paraffins that they follow the same classification. Although these olefins constitute an important part of refinery products, in no case are they present in natural gas.

The more important reactions which the natural-gas hydrocarbons undergo may be classified as follows:

(1) Cracking
(2) Oxidation
(3) Halogenation

The unsaturated hydrocarbons are much more reactive, and are, in addition, subject to:

(4) Addition
(5) Polymerization

Unfortunately the natural-gas hydrocarbons are very resistant to chemical changes, so that violent treatment must be resorted to in order to convert them into more desirable products. Methane, which is available in by far the largest quantities, is worst in this respect. There is a marked increase in reactivity in going from methane to ethane, while the difference between ethane and propane is not nearly as great, and butane is only slightly more reactive than propane. This relationship may be illustrated by taking the ignition temperatures given in Table I as a rough measure of the relative as well as actual reactivity of the lower paraffins. To initiate the combustion of methane in admixture with air, it is necessary to raise the temperature to 695–742° C. While ethane is ignited at 534–594° C., or an average of about

154° C. lower than methane, the average ignition temperatures for propane and butane differ only by 22° C.

TABLE I. IGNITION TEMPERATURES OF HYDROCARBONS IN AIR[a]

HYDROCARBON	IGNITION TEMP.
	° C.
Methane	695–742
Ethane	534–594
Propane	514–588
n-Butane	489–569
n-Pentane	476–548

[a] International Critical Tables, II, 173.

This great resistance to chemical changes of the gaseous paraffins, as compared with most other organic compounds, necessitates operation at temperatures where the products of reaction, as a rule, are exceedingly unstable. It also follows that the lower the hydrocarbon, the more difficult it becomes to stop the reactions at a specific point and to isolate the desired products. This has proved a most serious obstacle to the chemical utilization of methane, and the same difficulty is encountered even in the case of propane and butane, although to a lesser degree.

CRACKING

It has already been stated that the natural-gas hydrocarbons are remarkably stable to heat. Although free-energy calculations show that methane becomes thermodynamically unstable and tends to decompose to carbon and hydrogen at about 500° C., practical experience has shown that it is necessary to employ temperatures of 800° to 900° C., and above, to secure reasonably rapid decomposition. As the molecular weight increases, however, cracking takes place at successively lower temperatures.

The simplest and oldest process for thermal decomposition of natural gas is that employed in the manufacture of carbon black. The most common practice is to supply the necessary heat by incomplete combustion of the hydrocarbons. As would be expected, the efficiency is exceedingly low, being ordinarily between 2 and 5 per cent, depending upon the composition of the gas and the specific method of operation. By bringing the gas up to decomposition temperature by heat from an external source, yields as high as 40 per cent (*24*) have been obtained, and in this manner hydrogen is also produced, as illustrated by the equation:

$$CH_4 = C + 2H_2$$

The main outlet for the various types of black is the rubber industry, the daily production of this product in 1929 being somewhat over a million pounds. Although the carbon-black industry consumes more natural gas than all others put together (not including that used for fuel), the thermal decomposition to elementary carbon is a wasteful degradation which can hardly be considered an example of chemical utilization of the raw material.

By using less severe conditions, it is possible to crack selectively to unsaturated hydrocarbons, which may in turn be used as the starting point in the manufacture of various products. However, the great difference in reactivity of the natural-gas hydrocarbons makes it difficult to operate this type of cracking without previous separation. Propane, for example, will reach its maximum conversion to unsaturates long before methane begins to be attacked, and, if an attempt were made to operate at the temperatures and times of contact required for methane to decompose, the primary cracking products from any propane present would be entirely lost in secondary and tertiary reactions. In view of this and considering the widely different nature of the products, it is better to discuss the cracking of the various hydrocarbons separately.

METHANE. The temperature required to activate methane is so high that, when cracking first begins to take place, it is very difficult to avoid complete breakdown. By careful operation in the range of 800° to 1100° C., a certain amount of ethylene and acetylene may be obtained, but the commercial possibilities of this method cannot be judged on the basis of the data available (*15*). Another alternative is to crack at the much higher temperature of the electric arc, where the acetylene hydrocarbons formed are thermodynamically stable and may be recovered in good yields by rapid cooling of the reaction products. The results of recent experiments have verified the claims made in a series of patents to the I. G. Farbenindustrie (*16*) by showing that methane may be converted quantitatively into acetylene when cracked in an electric arc using a recycling system.

ETHANE. The data of Pease and Durgan (*30*) show that the equilibrium constant for the reaction

$$C_2H_6 = C_2H_4 + H_2$$

is equal to unity at about 800° C., and, since dehydrogenation of ethane takes place at a good rate in the range of 800° to 900° C., it is possible to crack to high yields of ethylene. Owing to secondary reactions, however, it is not practicable to go to complete conversion without employing a recycling system with removal of the ethylene between cycles.

PROPANE. A rather detailed discussion of propane cracking has recently been published by Schneider and Frolich (*32*). The main initial reactions are dehydrogenation to propylene and demethanation to ethylene:

$$C_3H_8 = C_3H_6 + H_2$$
$$C_3H_8 = C_2H_4 + CH_4$$

At lower temperatures the first reaction predominates, while ethylene formation is favored by high temperature. At 700° C. the two olefins are formed in equal amounts to the extent of about 90 per cent of the propane cracked. The remaining 10 per cent goes to various other products, notably ethane.

TABLE II. EFFECT OF PROGRESSIVE CRACKING ON PRODUCTS FROM PROPANE

(At 650° C.)

	COMPOSITION OF PRODUCT (PROPANE-FREE BASIS)	
	10% Cracking	80% Cracking
	%	%
C_3H_6	24.7	12.8
C_2H_4	21.6	29.4
CH_4	22.2	33.2
H_2	24.7	16.9
Others	6.8	7.7
Total	100.0	100.0

As the cracking progresses with increased time of contact, the initially formed propylene is rapidly consumed in secondary reactions, some of which lead to increased production of ethylene. This is illustrated by the data in Table II, which show the difference in composition of the products obtained by cracking propane to the extent of 10 per cent and 80 per cent at 650° C. In connection with the problem of further utilization of the olefins, it may be mentioned that the exit-gas mixture obtained by cracking, for example, 80 per cent of the entering propane at this temperature, can be fractionated readily into two cuts, containing, respectively, 35 per cent ethylene and 56 per cent propylene. The corresponding yields, based on the amount of propane actually cracked, are 58 per cent for ethylene and 25 per cent for propylene.

When carried out under the proper conditions, the cracking of the lower saturated hydrocarbons proceeds smoothly and without appreciable carbon formation. The process is being operated commercially on large scale for the purpose of obtaining ethylene and propylene as raw materials for the manufacture of various chemical products.

BUTANE. The reactions occurring in the cracking of butane have been studied by Hurd and Spence (*18*), who observed considerable difference in the products obtained from the two isomers. In the case of *n*-butane the major products are propylene and ethylene, formed according to the reactions:

$$C_4H_{10} = C_3H_6 + CH_4$$
$$C_4H_{10} = C_2H_4 + C_2H_6$$

With 22 per cent conversion at 600° C., the first reaction accounts for 55 per cent of the butane cracked and the second for 40 per cent. At higher temperatures, however, the ratio of ethylene to propylene increases, and in this respect the results resemble those already reported for propane cracking.

Isobutane gives chiefly isobutylene and propylene:

$$C_4H_{10} = C_4H_8 + H_2$$
$$C_4H_{10} = C_3H_6 + CH_4$$

For the same conversion at 600° C., the unsaturates produced consist of 51 per cent isobutylene, 39 per cent propylene, and only 8 per cent ethylene. As before, an increase in temperature favors formation of the lower olefins.

It is unfortunate that only a negligible amount of butylene is formed from *n*-butane, for this isomer seems to be available in preponderance. The writers have had experience with a natural gas from eastern Texas which contained *n*-butane and isobutane in the ratio 85:15. In refinery gases the ratio may vary considerably, depending upon the operations involved.

OLEFINS. In general, the olefins are more stable to temperature than the corresponding paraffins. This is rather fortunate because the olefins are valuable raw materials for the synthesis of various products, and it is therefore desirable to obtain them in high yields in the cracking of paraffins with the smallest possible loss to secondary products. However, on prolonged exposure to cracking conditions, the olefins do react with the formation of products which can be discussed more conveniently in connection with polymerization reactions.

OXIDATION

An enormous amount of research work has been done on the oxidation of the lower hydrocarbons for the purpose of obtaining valuable oxygenated derivatives preferably alcohols. It appears, however, that the initial oxidation products are so susceptible to further reaction at the temperature of operation that they are attacked by the oxidizing agent in preference to the original hydrocarbons, and, as a result of this, it is exceedingly difficult to obtain even moderately good yields. Bone's hydroxylation theory (*2*) postulates methanol as the primary product when methane is oxidized in air. Although there may be good reasons to believe that this is correct, very meager data are available showing that methanol can be produced by oxidation of chemically pure methane. Formaldehyde, representing the product of secondary oxidation according to Bone, may, on the other hand, be obtained in reasonable yields, provided the temperature is carefully controlled. It is also possible, by oxidation of a hydrocarbon such as butane, to obtain a mixture of a number of oxygenated compounds, including a small amount of alcohols with a lower number of carbon atoms. In general, the higher the hydrocarbon, the better the oxygen efficiency or yield of useful products, but at the same time the number of individual products increases. Pease (*29*) has shown that a considerable amount of olefins may be obtained by oxidation of butane with air at relatively high temperatures.

In spite of the many attempts made to introduce direct oxidation of gaseous hydrocarbons at ordinary pressure on a commercial scale, it is questionable whether there are any installations in operation at present. More promising results seem to be obtained by operation at high pressure. Lewis and Frolich (*25*) report results on oxidation of propane with elementary oxygen at pressures of the order of 2000 pounds per square inch (136 atm.) and temperatures around 300–350° C., showing that more than 40 per cent of the oxygen may be accounted for in the liquid organic oxidation products. The composition of a typical product is given in Table III. According to the explosive-limit determinations of Cooper and Wiezevich (*9*), it should be safe to operate with methane at a pressure of 3000 pounds (204 atm.) and temperature of 400° C. in the presence of less than 10 per cent oxygen. This figure may be raised somewhat in going to the higher gaseous hydrocarbons.

TABLE III. PRODUCT OBTAINED BY OXIDATION OF PROPANE WITH OXYGEN

[At 2000 pounds per square inch (136 atm.)]

	%
Acetaldehyde and acetone	6.0
Methanol	22.0
Ethyl alcohol (95%)	37.0
Propyl alcohol (78%)	7.0
Formic acid	1.5
Water	26.5
Total	100.0

Attempts have been made to oxidize hydrocarbons selectively to carbon monoxide and hydrogen, as exemplified by the reaction:

$$CH_4 + {}^1/_2O_2 = CO + 2H_2$$

However, in view of the high cost of elementary oxygen and the close temperature control required, it is questionable whether any process of this type has met with success. More satisfactory results are undoubtedly obtained by oxidation with steam:

$$CH_4 + H_2O = CO + 3H_2$$

This reaction goes very readily in the presence of a promoted nickel catalyst (*27*), but requires a large heat input at a high temperature level. It has been proposed to use the resulting gas mixture for the high-pressure synthesis of methanol (*19*),

$$CO + 2H_2 = CH_3OH$$

but with the present oversupply of methanol there is little incentive for expansion in this field. If hydrogen alone is desired, the carbon monoxide may be reoxidized with steam at a lower temperature by the use of a suitable catalyst,

$$CO + H_2O = H_2 + CO_2$$

the carbon dioxide being removed by scrubbing in known manner. It will be noted that 1 mole of methane yields a total of 4 moles of hydrogen by these two reactions. Two plants are now in operation in this country manufacturing hydrogen by this two-step process for use in high-pressure hydrogenation of petroleum products. The method may therefore be expected to find wider use with the growth of this industry.

HALOGENATION

Halogenation of the natural-gas hydrocarbons has met with only limited success, although a great deal of research has been done on reactions of the type:

$$CH_4 + Cl_2 = CH_3Cl + HCl$$

The main objection seems to be the difficulty of limiting the reaction to the introduction of only one chlorine atom per molecule of hydrocarbon, although this is largely a matter of temperature control (*4*, *23*). In view of the low cost of chlorine and the ease with which the alkyl halides are converted into other derivatives, such as alcohols,

$$RCl + H_2O = ROH + HCl$$

there should be considerable opportunities in this field. In many cases good yields of methyl chloride were obtained in the laboratory, but, when attempts were made to put the process on a plant scale, failure was inevitable. It seems to be somewhat easier to control the chlorination of the higher hydrocarbons; and alcohols, etc., have been manufactured from intermediates obtained by the chlorination of pentane on a commercial scale (*7*).

At present it is found more economical to prepare methyl chloride from beet-sugar residues. Carbon tetrachloride is prepared commercially by the interaction of carbon disulfide with sulfur dichloride, while chloroform is obtained by treating carbon tetrachloride with steam (*1*).

Of the many outlets which have been proposed for the lower alkyl chlorides, the addition of carbon monoxide to form acid chlorides is of interest:

$$CH_3Cl + CO = CH_3COCl$$

The writers have found this reaction to proceed at 700–800° C. with an efficiency of over 75 per cent, although the yields per pass are limited. Various catalysts for this reaction have been mentioned in a patent to the I. G. Farbenindustrie (*21*).

Addition Reactions

Theoretically it should be possible to obtain a variety of products by direct additions to the rather reactive unsaturates already available in refinery gases, or formed by the cracking processes discussed in a previous section. However, only those reactions on which a reasonable amount of experimental data are available will be discussed here.

Chlorine and Chlorine Derivatives. The direct addition of elementary chlorine to unsaturated hydrocarbons, as illustrated by the formation of ethylene dichloride,

$$C_2H_4 + Cl_2 = C_2H_4Cl_2$$

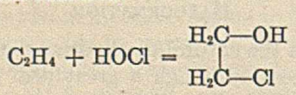
proceeds so readily that products of this type can be manufactured without difficulty at low cost. The problem here is to find suitable outlets for the chlorinated compounds, either as solvents or as intermediates for use in the synthesis of other derivatives.

It has also been claimed in the patent literature (*31*, *36*, *38*) that hydrochloric acid may be added to olefins, for example, by the aid of pressure:

$$C_2H_4 + HCl = C_2H_5Cl$$

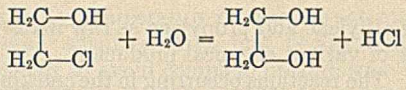
There is no reason to doubt that such reactions can be made to go almost quantitatively, and the indications are that it will prove more economical to manufacture lower alkyl chlorides in this manner than by chlorination of the paraffins. The main problem here is to find uses for these materials also.

Finally, it is possible to add hypochlorous acid to olefins, as exemplified by the reaction:



$$C_2H_4 + HOCl = \begin{array}{l} H_2C-OH \\ \;\;| \\ H_2C-Cl \end{array}$$

This process has the advantage that the chlorine atom is easily replaced by other groups to form new derivatives. The reaction given above may, for example, be followed by hydrolysis to give ethylene glycol (*10*, *12*):



$$\begin{array}{l} H_2C-OH \\ \;\;| \\ H_2C-Cl \end{array} + H_2O = \begin{array}{l} H_2C-OH \\ \;\;| \\ H_2C-OH \end{array} + HCl$$

In this manner ethylene glycol and a large number of other derivatives of ethylene suitable as solvents and plasticizers have for some time been manufactured commercially in this country (*11*).

One addition reaction, which has been claimed to be relatively simple to effect, is the addition of phosgene to ethylene with the resulting formation of chloropropionyl chloride (*28*):

$$C_2H_4 + COCl_2 = CH_2Cl \cdot CH_2COCl$$

Although a large number of experiments have been made in this laboratory on such a process, no indications of any appreciable amounts of the acid chloride have been found.

Water and Alcohols. Thermodynamic calculations indicate that it should be possible to produce alcohols by addition of water to the olefins. The low reactivity of such a mixture should be no handicap, for the existing free-energy data show favorable equilibrium conditions even at temperatures as high as 400° to 500° C., provided pressures of several hundred atmospheres are used. In spite of this, however, and contrary to the claims of the patent literature, the results obtained by Swann, Snow, and Keyes (*35*) on the direct hydration of lower olefins under high pressure show only negligible yields. The writers' experience in this field has also been discouraging, in that the conversions obtained have not approached anywhere near the calculated figures. On the other hand, the production of alcohols may be carried out successfully by adding water to olefins by way of their sulfuric acid esters:

$$C_nH_{2n} + H_2SO_4 = C_nH_{2n+1}\,OSO_3H$$
$$C_nH_{2n+1}\,OSO_3H + H_2O = C_nH_{2n+1}\,OH + H_2SO_4$$

By absorbing the corresponding olefins from refinery gases in sulfuric acid of the proper concentration followed by hydrolysis with water, isopropyl and higher secondary alcohols are manufactured commercially in large quantities by this process. By treating the sulfuric acid esters with calcium acetate, the corresponding acetates may also be produced directly by the process of Ellis and Cohen (*13*), as exemplified by the formation of isopropyl acetate:

$$2C_3H_7OSO_3H + (CH_3COO)_2Ca = 2CH_3COOC_3H_7 + CaSO_4 + H_2SO_4$$

This process is also being operated on a commercial scale. Isopropyl alcohol so formed may likewise be used as a starting material for preparing such compounds as propyl chloride (*5*), chloroacetone (*6*), acetone (*37*), etc.

It has been mentioned in previous sections that water may also be added indirectly to give alcohols and glycols by hydrolysis of intermediately formed chlorine derivatives.

Acetylene has been successfully hydrated to acetaldehyde (*20*), and this compound has been the starting point for the preparation of numerous compounds, such as acetic acid, acetic anhydride, acetone, etc. Acetic acid is prepared commercially by this process, although the acetylene used is obtained from calcium carbide rather than from hydrocarbons.

A recent development in this field is the production of acetic anhydride from ethylidene diacetate (*3*, *26*). Acetylene first reacts with acetic acid to produce ethylidene diacetate, which is then thermally decomposed in the presence of a catalyst, yielding acetic anhydride and acetaldehyde:

$$C_2H_2 + 2CH_3COOH = CH_3CH(OCOCH_3)_2$$
$$CH_3CH(OCOCH_3)_2 = (CH_3CO)_2O + CH_3CHO$$

The acetaldehyde so produced is oxidized to acetic acid for use in the process.

Acetals have been prepared by the interaction of acetylene with alcohols (*8*) in presence of mercury catalysts, presumably according to the equation:

$$C_2H_2 + 2CH_3OH = CH_3CH(OCH_3)_2$$

The yields are claimed to be in the neighborhood of 65 per cent.

AMMONIA. Amines do not seem to be formed very readily by direct addition of ammonia to olefins:

$$C_nH_{2n} + NH_3 = C_nH_{2n+1}\,NH_2$$

Although free-energy calculations indicate favorable equilibria, and although good results have been obtained with aromatic halides (*17*), only small yields were obtained in a study of this reaction covering a wide variety of catalysts at pressures up to 3000 pounds (204 atm.). It may be, however, that the solution lies in the development of the proper catalysts.

POLYMERIZATION

A great deal of attention has been given lately to the problem of hydrocarbon polymerization. Besides a prolific patent literature on the subject, there have been a number of publications dealing with the polymerization of olefins, as well as the simultaneous cracking and polymerization of natural-gas hydrocarbons. In general, it may be said that the attempts to produce hydrocarbons of high molecular weight by combined cracking and polymerization of the lower ones have not as yet given as satisfactory results as might have been desired. The reason for this is mainly the difficulty experienced in controlling the process and stopping the reactions at the desired point. At the high temperature required for the initial cracking reactions to take place, the polymerization products are decidedly aromatic in character, but unfortunately the reactions proceed beyond the stage of liquid materials, and yield a heavy tar as the final product. The highest yields of benzene and other products suitable as motor fuel, obtained in a one-step process, are therefore about 0.4 to 0.6 gallon per thousand cubic feet (54–80 cc. per cubic meter) of methane and 1.5 to 2.0 gallons (200–268 cc.) in the case of propane. In view of the high temperature of operation (700–1000° C.), and the necessity of employing recycling with cooling and condensation of the heavily diluted products in between cycles, it would be impracticable to operate such a process commercially at present.

A better method of attack is to crack and polymerize in separate steps, because this makes it possible to choose the most favorable operating conditions for each process. These conditions are high temperature and short time of contact for the cracking process, followed by long time of contact at lower temperature for the polymerization. The best results are obtained by polymerization under high pressure, after the hydrogen formed in the initial cracking step has been removed, for example, by selective oxidation over a suitable catalyst. Depending upon the temperature and pressure used in the polymerization, it is possible to vary the composition of the product within wide limits, i. e., from typically aromatic to a naphthenic character (*14*). By this method of polymerization, almost quantitative yields of liquid material have been obtained from relatively pure ethylene, propylene, and butylene. As another example, it may be mentioned that the two-step process has given about 10 gallons of product per thousand cubic feet of propane (1.34 liters per cubic meter). On a carbon basis, this corresponds to 65 per cent conversion of the original propane to liquid hydrocarbons. Of this material some 80 per cent boiled in the gasoline range, and, when this fraction was blended in gasoline to the extent of 20 per cent, the lowering in knock rating was 75–85 per cent of that produced by an equivalent amount of benzene. In spite of these results it is questionable whether a process of this type could compete under the prevailing market conditions.

Some interesting results on the polymerization of olefins in presence of aluminum chloride have been reported by Sullivan and others (*34*). Oils possessing good lubricating properties were obtained in this way from olefins of high molecular weight, but in the case of the gaseous olefins the oils produced had unsatisfactory viscosity-temperature relationships, making them unsuitable as lubricants.

Before leaving this subject it may be mentioned that diolefins are intermediate products in the formation of aromatics by polymerization of the lower olefins at high temperature (*32*). It has been found, for example, that ethylene may be converted into butadiene,

$$2C_2H_4 = C_4H_6 + H_2$$

with an initial efficiency of 70 per cent. Whether or not reactions of this type will ever attain commercial importance depends largely upon whether it will be possible to isolate the diolefins before the reaction has had a chance to go beyond this point. Cheap diolefins would be a suitable raw material for the manufacture of rubber and other amorphous solids. By subjecting mixtures of acetylene and ammonia to 250–500° C., pyridine and other heterocyclic bases are claimed to have been prepared (*22*, *33*), indicating that during the polymerization the nitrogen can be made to enter the ring.

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Bright Annealing of Metals with Hydrocarbon Gases

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THE CORROSION of material in general and the corrosion of metals in particular has received great attention, owing to its obvious economic importance. Attention for the most part, however, has been focused on the corrosion of metals under atmospheric conditions. Relatively little thought has been devoted to the corresponding corrosion problem which occurs during almost all high-temperature operations involved in the preparation of metals for industrial purposes. Typical of such operations are those of annealing, normalizing, forging, etc. Under the conditions of these processes, corrosion or oxidation proceeds far more rapidly than atmospheric corrosion and is of no less economic importance. In this paper the authors are concerned with one aspect of the general problem—the prevention of oxidation of metals during the process of annealing.

THE problem of the bright annealing of metals is essentially a chemical one. It is perhaps owing to the fact that combustion and heating operations have in the past been considered the province of the power engineer or the mechanical engineer that certain of the more involved chemical problems attendant upon, or arising out of, industrial heating operations have not received the attention that their economic importance merits. It is, of course, well known that metals vary greatly in the ease with which they combine with oxygen at high temperatures. Silver, for example, may readily be heated at high temperatures in an atmosphere that would rapidly oxidize iron, without the occurrence of any appreciable amount of oxidation. To the chemist, the more precise statement of these observations is that the free energy of formation of the oxides decreases as the electromotive series of the metals is descended. For these reasons some metals may be maintained bright very easily during heat treatment, the only requirement being that no free oxygen shall be present in the atmosphere. This is generally accomplished by using raw gas or the products of combustion in a muffle furnace. In some cases steam is employed, and this generally has proved moderately satisfactory for the bright annealing of copper.

In a previous paper by the authors (*1*) a general survey was given of the reactions occurring between metal surfaces and the gases available industrially for high-temperature furnace operations. The difficulty of heat-treating copper-zinc alloys, usually included in the generic term "brass," was emphasized. At low temperatures the difficulties encountered are not great, but, as the temperature is increased to desired annealing temperatures and where zinc begins to volatilize from the surface, the difficulties are multiplied. The volatilization of zinc seems to be coincident with the liberation of occluded gases. These gases are oxidizing to the metal and results in the formation of a scale on the surface of the metal, consisting either of zinc oxide or a mixture of oxides. Thus the metal becomes tarnished and the problem of bright annealing is greatly complicated.

The usual method of approach to this problem has been to employ various atmospheres that are commonly considered neutral or reducing in their action. In gas-fired furnace technic the attempt has been made to use a purified flue gas. To do this, it has been necessary to remove the water vapor and carbon dioxide, since both of these are highly oxidizing to heated brass. This leaves a nitrogen atmosphere containing small amounts of carbon monoxide. Such attempts have not succeeded in producing a bright-annealed brass, owing primarily to the oxidizing gases liberated from the metal itself. In a recent contribution on this subject (*2*) the authors have presented experimental evidence to show that neither pure nitrogen nor, in fact, pure carbon monoxide will prevent the staining and scaling of brass during the annealing process. In that paper the authors were also able to prove experimentally the fact that relatively small amounts of methanol vapor added to atmospheres that were highly oxidizing to brass would, however, completely prevent the formation of oxide films on the metal surface. The phenomena observed could be accounted for on the assumption that the methanol vapor was acting as an inhibitor to the oxidation reactions. The mechanism of this inhibitory action was not determined, but it is not improbable that it was brought about by the selective adsorption of the methanol vapor on the metal surface.

In continuing the experimental investigation of these phenomena, it has been found that under proper conditions the bright annealing of metals, and particularly of brasses, can be accomplished in an atmosphere of hydrocarbon gases. The underlying phenomena which make this bright-annealing process possible are apparently not limited to hydrocarbon gases but may be obtained by employing any gas which will liberate hydrogen, or, in fact, hydrogen itself under properly controlled conditions.

EXPERIMENTAL PROCEDURE

Brass wire of 18 gage was threaded through a laboratory tube furnace on a reeling device that made it possible to control the rate of travel through the hot zone. Hydrocarbon gases were introduced along the furnace tubes at particular points and made to flow in the desired direction by controlling the pressure at various points in the tube. The flow of gas, the temperature of the furnace, and the speed of travel of the metal wire were controlled by the usual methods. The wire employed was initially constant throughout as to composition, hardness, and grain structure.

The hydrocarbon gases employed were methane (natural gas), ethane, propane, butane, ethylene, and acetylene. All of these gases behaved substantially alike so far as the results pertinent to this investigation are concerned. Analyses of the gases issuing from the furnace were made where the information was necessary for the interpretation of results. In such cases a standard United States Steel gas-analysis apparatus was employed.

RESULTS

The initial series of experiments indicated that, unless the furnace was heated to a temperature equal to or in excess of 1250° F. (676.7° C.), the brass wire could not be made bright even in the hot zone itself. Perhaps it should be mentioned that the wire could be satisfactorily annealed at lower temperatures, but in such cases the surface was always found to be badly oxidized or coated. It was also found that, when the hydrocarbon gas was fed into the furnace countercurrent to the movement of the metal, the surface of the metal was always oxidized, even though observation showed that it had been rendered bright in the hot zone maintained about 1250° F. (676.7° C.). This fact threatened to prove an obstacle to the practical operation of the process, since, if the gas were made to flow countercurrent to the work, the latter would tarnish as it advanced to meet the inflowing gas. On the other hand, if the gas were made to flow concurrent with the metal, air would be drawn in along with the metal, giving rise to the probability of tarnishing the surface as it cooled in the process of reaction.

However, as the temperature to which the hydrocarbon was exposed before coming into contact with the metal was raised, it was found that, if the gas was exposed to a temperature of about 1250° F. (676.7° C.) before contacting with the metal, no tarnishing occurred. At this temperature a pronounced cracking of the gas had occurred, resulting in the precipitation of a small amount of carbon and the production of hydrogen. The amount of this cracking, of course, was a function of the hydrocarbon employed and the catalytic effect of the tube walls. It was observed further that, unless this cracking occurred, a bright anneal could not be obtained. For example, a glass muffle had so little catalytic effect on the decomposition of methane that in this case no observable cracking occurred at 1250° F. (676.7° C.) under the conditions of the experiment. Under this condition it was found that the surface of the brass could not be rendered bright until a temperature of 1450° F. (787.7° C.) was employed, at which temperature an appreciable amount of cracking occurred. In the case of acetylene, on the other hand, cracking occurred at temperatures appreciably lower than 1250° F. (676.7° C.), yet it was found necessary to subject the gas to this temperature before the surface of the brass could be maintained bright.

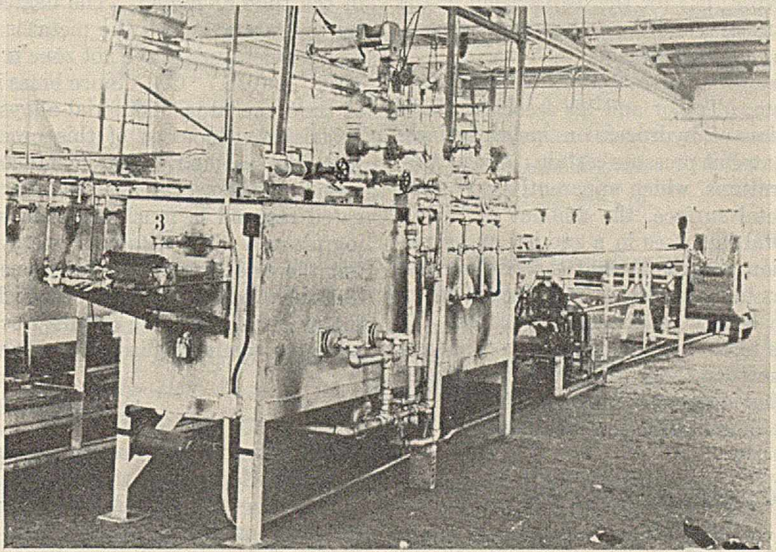
FIGURE 1

These results appeared to indicate that, in order to obtain a bright surface at a temperature equal to or above the desired annealing temperature of the brass, it was necessary to accomplish two things. Some cracking of the hydrocarbon must have taken place, and the gas itself must have been exposed to a temperature of at least 1250° F. (676.7° C.). When the gas was in such condition as to avoid tarnishing the metal, it was then in a condition to bright anneal properly. What is termed here the "bright-annealing reaction" has distinctive and characteristic effect. It is very definitely a reaction on the metal surface whereby the metal becomes brilliant in luster and superior in appearance to its original condition. When hydrocarbon gases are employed, this reaction is only accomplished when the two criteria just mentioned have been met.

MECHANISM OF BRIGHT-ANNEALING REACTION

In order to determine more precisely the mechanism of the bright-annealing reaction, the attempt was made to determine whether the phenomena observed were due to a transient intermediate compound formed during the decomposition of the hydrocarbon or to the formation of hydrogen alone. The results already described seem clearly to indicate that the hydrocarbon itself was not responsible for the bright-annealing reaction. Accordingly a series of experiments was conducted, using pure hydrogen alone in place of the hydrocarbon gas.

Confirming results previously reported by the authors, it was found that pure hydrogen does not produce a bright anneal at the usual brass-annealing temperature of 1000° F. (537.8° C.). If a piece of brass be heated in such an atmosphere and observed during the heating, it will be seen to tarnish at temperatures around 800° F. (426.7° C.). There is no indication of bright annealing, short of 1200° F. (648.7° C.). At this point, however, the reaction proceeds rapidly, and a beautiful metal surface is produced. Below this point the gas seems to be inert. This temperature therefore must be either the temperature at which the reaction system must be raised in order to obtain a sufficiently rapid reduction of oxides, or else it must be the temperature at which hydrogen must be brought to activate it so that the reduction of oxides may proceed.

Now it is of some importance to be able to bright anneal brass without raising the temperature of the metal itself to 1250° F. (676.7° C.) or above. In many cases to do so would result in an overannealed condition with a consequent grain growth that would be objectionable for some industrial purposes. That the temperature of 1250° F. (676.7° C.) was not the minimum temperature which the metal itself had to obtain in order that deoxidation might proceed, was proved by the following results. When brass is heated to a definite temperature, its structure reveals a definite grain size corresponding to this temperature. By this means it was found possible to approximate very closely the temperature which the brass had attained on being passed continuously through the heated muffle. A simple comparison of the grain size of the sample with the grain size of similar samples subjected to known temperatures suffices to accomplish this. Using this method, it was found that brass could be bright annealed at lower temperatures—800° to 900° F. (426.7° to 482.2° C.) in pure hydrogen if the hydrogen itself were heated to 1250° F. (676.7° C.) or above. These temperatures were obtained by passing the metal through the hot zone at such a rate that it could reach only the desired metal temperature. If the temperature of the hot zone, that is the temperature of the hydrogen, were less than 1250° F. (676.7° C.), the reaction did not take place. The point to be emphasized clearly is that apparently the metal oxides could be reduced readily at temperatures below 1000° F. (537.8° C.) if the hydrogen itself was at a temperature in excess of 1250° F. (676.7° C.), and that reduction apparently did not occur if the hydrogen temperature was below 1250° F. (676.7° C.).

These results seem to contain considerable evidence that the bright-annealing reactions were brought about by hydrogen in some particular condition or state of activation. Further evidence of this fact was noted when ammonia was substituted for hydrogen. The results obtained were quite similar to those with hydrocarbon gases. The ammonia dissociates somewhat more readily in the iron tubes employed than do the hydrocarbons. Nevertheless it was found that not only must dissociation have taken place with the consequent liberation of hydrogen, but that the products of dissociation must have attained a temperature of approximately 1250° F. (676.7° C.) for the deoxidation of the metal surface. Under these conditions, however, a very satisfactory bright anneal can be obtained.

Certain recent work by other investigators (*3*) may have a bearing on this problem. Taylor and his associates have found that the adsorption of hydrogen on metal surfaces does not follow a simple law but presents certain complexities. At fairly definite temperatures, which apparently vary with the condition of the metal surface, the amount of hydrogen adsorbed by the metal increases in a sudden and striking way. One explanation given is that at the critical temperature some change has taken place in the hydrogen which enables it to pack more closely on the metal surface. To be sure, the observations made by Taylor et al. were at temperatures very much lower than those with which the present authors have dealt. This difference may possibly be explained by the different character of the metal surface employed in each case.

CONCLUSION

As a result of this investigation a process for the bright annealing of metals has been developed which is applicable to industry. Apparently any gas which is not deleterious to the metal, and which will serve as a source of hydrogen may be employed. Pure hydrogen itself may be used, but it has certain severe limitations. Not only is its explosibility a drawback but its use increases the volatility of zinc when the metal being annealed is brass. Comparative tests indicated that there was a loss of 1.8 per cent of the weight of brass sheets when annealed in a hydrogen atmosphere, as compared to a loss of 0.72 per cent under similar conditions when the annealing atmosphere was methanol and flue gases.

Apparently hydrocarbon gases will prove the cheapest and most available raw material for this bright-annealing process. With their use it is possible to produce the desired amount of hydrogen under suitably controlled conditions. The ready availability and ease of handling of these gases renders them particularly attractive for commercial operation.

The details and the practical operation of this process have been worked out, and it has been adapted to the bright annealing of many different metals and alloys. The metal is passed through a tube furnace in the form of wire or strip. Seals are provided at each end of the furnace, and the hydrocarbon gas is admitted through inlets suitably situated in the tube or muffle. The degree of anneal is determined by the rate at which the metal is moved through the tube. The temperature of the hot zone is maintained slightly above 1250° F. (676.7° C.). Since brass is one of the most difficult of the more usual industrial alloys to bright anneal, the industrial development of this process has been approached with the peculiar requirements of brass in view. It has been found, however, that all other metals and alloys investigated respond in much the same way to the bright-annealing process. The details of operation vary with each metal, but the essentials of the reactions are the same. Figure 1 illustrates a type of furnace which has been developed for the practical operation of this process. Steps are now being taken to commercialize its applications.

ACKNOWLEDGMENT

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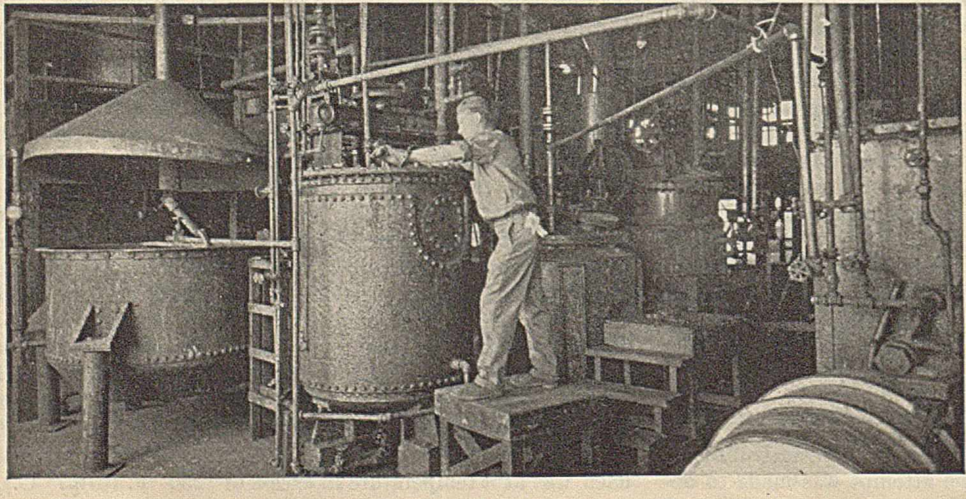

A corner in a modern dye plant showing equipment typical of that used in the manufacture of vat dyestuffs.

Courtesy, E. I. du Pont de Nemours & Co., Inc.

Thermatomic Process for Cracking of Gaseous Hydrocarbons

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THE thermal decomposition of a gaseous hydrocarbon, such as methane, in the absence of air produces carbon and hydrogen according to the equation:

$$\mathrm{CH_4}\ \text{(upon heat cracking)} \longrightarrow \mathrm{C} + 2\mathrm{H_2}$$

Theoretically from every thousand cubic feet of methane thus treated 31.82 pounds of carbon are formed as well as 2000 cubic feet of hydrogen. In order to create sufficient heat to carry on this cracking, which is an endothermic reaction, part of the methane, or gaseous hydrocarbon being used, must be burned with air to heat the system to cracking temperature. The portion consumed for this purpose depends on the process used as well as on the efficiency of operation. The amount of carbon entrained during the decomposing period and the space velocity are also important factors. So much has been written on the subject of this reaction that it hardly seems necessary to elaborate further here (*2, 3, 6, 8–11, 15, 18*).

THE PROCESS may be described in four parts—namely, (1) the cracking units, consisting of checkerwork furnaces, (2) the coolers, (3) the carbon collectors, and (4) packing. The furnaces being used at present are 14 feet in diameter and 25 feet high, and consist of a riveted steel shell, insulated and lined with refractory brick and filled with checkerbrick, similar to a blast-furnace stove. The temperature range in the furnace is from 900° to 1400° C. The process is intermittent, the checkerwork being first heated by a blast of natural gas and air introduced at the bottom, after which the stack is closed and natural gas is added from the top of the furnace for the decomposing part of the cycle.

The smoke from the furnace is passed through a cooler chamber where sufficient water is sprayed countercurrent to the gas stream to cool the smoke sufficiently to allow it to be safely filtered through the cloth bags in the collectors and yet not wet either the bags or the carbon.

A typical chemical analysis of the natural gas being used at the Sterlington, La., plant, and the resultant gas obtained therefrom is as follows:

	VOLUME NATURAL GAS	VOLUME RESULTANT GAS
	%	%
Carbon dioxide	0.4	0.9
Illuminants	0.7	1.3
Hydrogen	..	85.4
Carbon monoxide	..	1.1
Methane	93.8	5.0
Nitrogen	5.1	6.3

A general arrangement of the equipment is seen in Figure 2 (*23*).

The furnaces being used at present are 14 feet in diameter and 25 feet high, and consist of a riveted-steel shell, insulated and lined with refractory brick and filled with checkerbrick, similar to a blast-furnace stove. The temperature range in the furnace is from 900° to 1400° C. The process is intermittent, the checkerbrick being first heated by a blast of natural gas and air introduced at the bottom, after which the stack is closed, and natural gas is added from the top of the furnace for the decomposing part of the cycle.

The smoke from the furnace is passed through a cooler chamber where water is sprayed countercurrent to the gas stream (*20*) to cool the smoke sufficiently to allow it to be safely filtered through the cloth bags in the collectors and yet not wet either the bags or the carbon.

The collectors (*22*) comprise a battery of cotton bags enclosed in a steel shell with hoppers underneath. The collectors are built along the general principles of the dust collectors commonly used by the powdered-coal and starch industries, and have been highly successful. The smoke enters a bag through the bottom; this open end of the bag is clamped tightly to a flange in a steel plate which separates the upper shell of the collector and the hopper. The upper end of the filter bag is shaken intermittently by an air-hammer device. During this period the flow of gas is shut off from the shaking bags, and the carbon falls from the cloth into the hopper. The filtered resultant gas is piped off from the top of the collectors.

After the carbon falls into the hoppers, it is then carried by screw conveyors to the sifters. Just ahead of the sifters are magnetic separators which clean out any metallic scale or rust which might possibly come off the collector hoppers or conveyors. The carbon is then air-floated through fine-mesh wire screens. Large rotors with rubber flippers attached throw the carbon centrifugally through the screening. From the sifters the carbon falls into the packing hoppers where it is accurately weighed and packed in 30-pound paper bags.

The above description is of the process which produces the Thermax brand of Thermatomic carbon. This is the pioneer "soft" carbon, having been produced commercially in Louisiana since 1922 by the thermal decomposition of natural gas. Recently a new improved brand, called P-33, has been put on the market. This carbon is blacker and finer than Thermax and is also a soft carbon. It is made by a process essentially the same as Thermax, the difference being that, in making P-33, a portion of the resultant gas is recirculated and acts as a diluent for the natural gas being decomposed, thereby allowing the particles of carbon to be formed in a more dilute atmosphere (*4*). This dilution principle is so effective as to reduce the average particle size of P-33 to about one-fifth that of Thermax.

In the study of the patent literature pertaining to the manufacture of carbon, one is struck by the fact that most processes are described quite fully, and the product formed is merely mentioned as a soot or a lampblack. The fact that the carbons produced from hydrocarbons differ widely in their physical properties and effect on rubber, paint, oils, etc., has led to the publication recently of several articles on the subject (*1, 5, 7, 12, 14, 16, 17, 19*). In these articles reference is made to "Thermatomic carbon," which, in all cases where named, is what is now known as Thermax brand.

By the term "soft" carbon is meant one which, when added to rubber in any appreciable quantity, does not increase the modulus (tensile strength at either 300 or 500 per cent elongation) of the vulcanized rubber stock in a measure comparable to that obtained with an equal quantity of channel carbon black (*13, 21*). The term as used in the literature refers to the influence of the carbon on the vulcanized stock and not to either the carbon itself or the uncured rubber stock. Tables I and II illustrate the difference in physical properties produced in rubber by channel black and P-33 carbon.

Thermax has established itself in the rubber trade throughout the world and is being successfully used in tires, inner tubes, boots and shoes, hose, belts, and other mechanical goods. It improves the working or processing qualities of compounds containing large quantities of reclaim and, in fact, has been added to reclaim itself for the same reason. It is also being used in paints, automobile-top fabrics, carbon brushes, and electrodes.

P-33 carbon, as previously stated, is blacker and has a much smaller average particle size than Thermax. It imparts practically the same stiffening effect to rubber as Thermax,

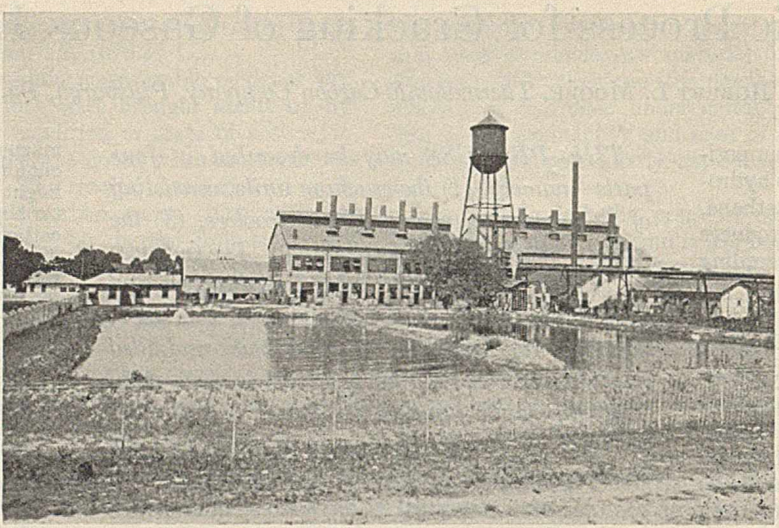

Figure 1. Sterlington, La., Plant of Thermatomic Carbon Co.

but reinforces rubber to a greater extent. The ultimate tensile strengths obtained closely approach those imparted by using equal loadings of channel black. The resistance to tear of rubber stocks compounded with P-33 carbon is high, and because of this and the low modulus this new product is finding considerable use in high quality heat-resisting inner tubes, hose and belt covers, tire carcasses, and rubber stocks where high concentrations of pigment are desirable. For example, equal parts of rubber and this carbon make a resilient pliable stock suitable for many purposes in mechanical goods. One of the most important uses for P-33 carbon has been in the newer types of lacquers and dipping enamels for the automotive, electrical, and hardware industries. Because of its blackness and low oil absorption, it has been possible to grind the carbon more easily and disperse it better in these very thin paints.

Table I. Formulas

	A	B
Smoked sheet rubber	100.00	100.00
Diphenylguanidine	1.25	0.70
Sulfur	3.50	3.50
Zinc oxide	5.00	5.00
Channel carbon black	40.00	...
P-33 carbon	...	40.00

A comparison of the physical and chemical properties of Thermax and P-33 are given in Table III.

The gas produced by the Thermatomic process is of especial importance at the present time because of the interest in the hydrogenation of petroleum, the reforming of natural and refinery-still gases, as well as the synthesis of ammonia and methanol. This gas can be readily produced at any location desired from any gaseous or liquid hydrocarbon and does not present any new problems in purification. The fact that the cracking units are long-lived and free from troublesome complications of operation has been proved by nine years of commercial production with natural gas in Louisiana where over 100 million pounds of carbon and 12 billion cubic feet of hydrogen have been manufactured.

Table II. Stress-Strain Data

	Cure at 141° C.	Tensile Strength at: 300% Elongation		Tensile Strength at: 500% Elongation		Tensile Strength at Break		Ultimate Elongation
		Kg./sq. cm.	*(Lb./sq. in.)*	*Kg./sq. cm.*	*(Lb./sq. in.)*	*Kg./sq. cm.*	*(Lb./sq. in.)*	%
A (Channel)	30	67	(950)	189	(2700)	310	(4400)	645
	45	91	(1290)	222	(3190)	329	(4680)	620
	60	104	(1480)	247	(3510)	334	(4750)	590
	75	118	(1675)	263	(3750)	319	(4540)	560
B (P-33)	30	28	(400)	102	(1450)	315	(4480)	760
	45	35	(500)	124	(1770)	323	(4600)	735
	60	42	(600)	135	(1920)	322	(4590)	725
	75	42	(610)	144	(2050)	305	(4340)	680

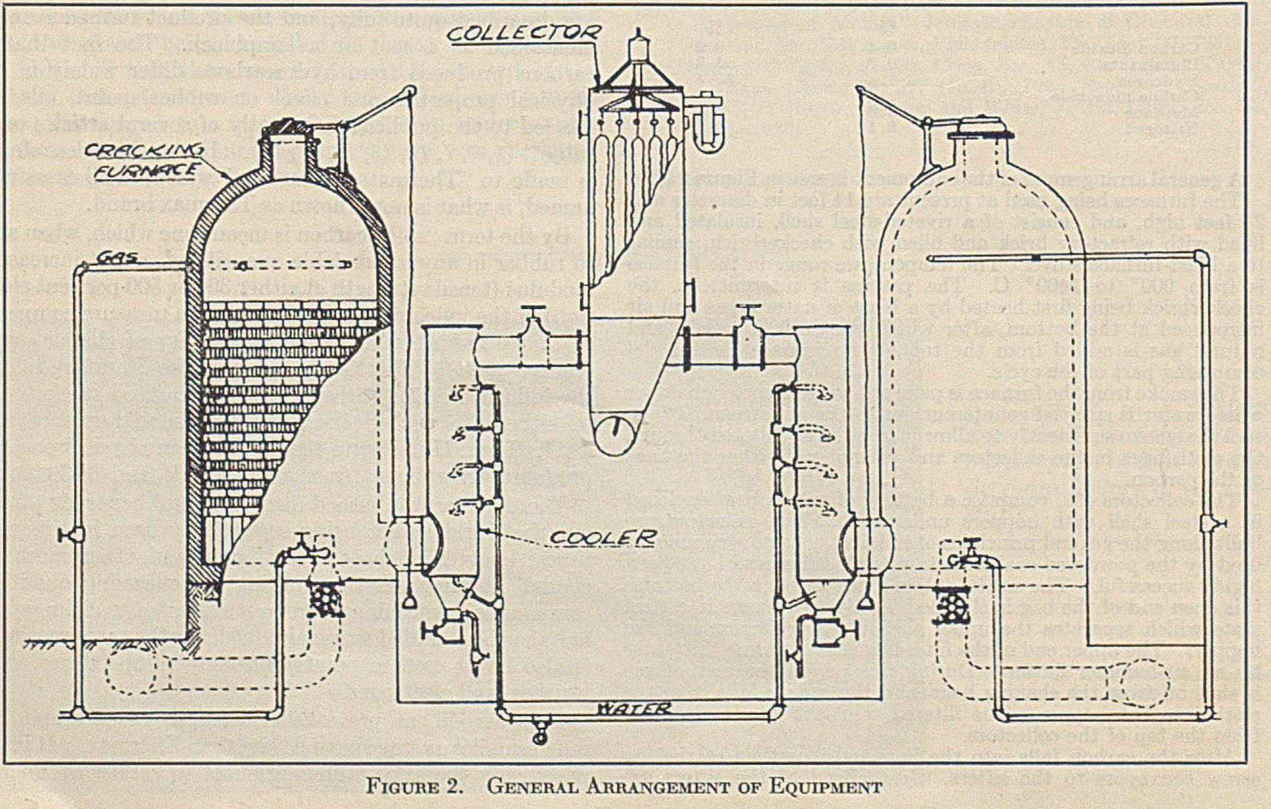

Figure 2. General Arrangement of Equipment

TABLE III. PROPERTIES OF THERMAX AND P-33 CARBON

	THERMAX	P-33
PHYSICAL		
Specific gravity	1.80	1.80
Apparent gravity (bulking value), kg./cu. meter	481.5	356.1
(lbs./cu. ft.)	(30)	(22)
Tinting strength,[a] %	14	50
Average particle size, micron	1.0[b]	0.23[c]
CHEMICAL		
Moisture, %	0.25	0.25
Ash, %	0.05	0.15
Benzol extract (16 hours' extraction), %	0.60	1.25

[a] Determinations made with Keuffel and Esser color analyzer at a concentration of 2.5 parts carbon to 100 parts zinc oxide. (Cabots Certified Carbon = 100%.)

[b] Average of 2000 counts at 1940 diameters magnification.

[c] Average of 1000 counts at 1940 diameters magnification.

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Conversion of Methane to Carbon Monoxide and Hydrogen

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A CYCLIC process has been developed for converting methane, or gases containing methane, to carbon monoxide and hydrogen by either of two reactions with equally satisfactory results:

$$CH_4 + H_2O \longrightarrow CO + 3H_2$$
$$CH_4 + CO_2 \longrightarrow 2CO + 2H_2$$

The process is one in which the heat of reaction is supplied to the gases by the catalyst bed, heated to reaction temperature by blasting with an air-gas flame. Catalysts can be prepared for this purpose which are quite durable, and will consistently produce conversions near the calculated equilibrium values.

Optimum experimental conditions have been determined for producing maximum conversions and minimum contamination by the products of side reactions in the temperature range 900° to 1100° C.

THE conversion of hydrocarbons, especially methane (in natural or coke-oven gas), to carbon and hydrogen or to mixtures of carbon monoxide and hydrogen constitutes a problem which has already received considerable attention in the industrial world. Methane, although thermodynamically unstable at temperatures as low as 550° C., does not thermally decompose rapidly except at very much higher temperatures (1100–1300° C.). The United States Bureau of Mines has investigated the thermal decomposition of natural gas in the presence of incandescent carbon, in water-gas generators at high temperatures, with and without the presence of steam (*6*). With the addition of steam, this reforming process is satisfactory for the production of fuel gas, but, for the conversion of methane to carbon monoxide and hydrogen for synthetic purposes, it is complicated by the appearance of side reactions whose end products are tarry substances, mixtures of simpler liquid hydrocarbons, and heavy members of the benzene series.

The reactions by which methane may be converted to mixtures of carbon monoxide and hydrogen are as follows:

$$CH_4 + H_2O \longrightarrow CO + 3H_2 \quad (1)$$
$$CH_4 + CO_2 \longrightarrow 2CO + 2H_2 \quad (2)$$

Both of these reactions are highly endothermic. By similar reactions higher hydrocarbons may also be decomposed to give the same products. A consideration of the thermodynamic properties of the methane reactions shows that, in the case of methane and steam used in the proportions of Reaction 1, the process must be carried out at temperatures at least as high as 900° C. to obtain satisfactory conversions. The free energy and equilibrium constants for this reaction at various temperatures, calculated from free-energy data made available by the work of Eastman (*3*) and Storch (*8*) have the following values:

$T°$ K.	1,073	1,173	1,273
ΔF	−10,700	−16,722	−22,735
K_p	150.5	1.296×10^3	0.794×10^4

An approximate calculation of the concentration of the various constituents in the equilibrium mixture at 900° C. shows the methane content of the gas to be somewhere near 1 per cent, which corresponds to about 96 per cent conversion of the original gases. Reaction 2 approaches completion more rapidly than Reaction 1, with increasing temperature; but again an approximate calculation of the proportions of the constituents of the equilibrium mixture at 900° C. shows that the conversions to be expected are of the same order as in Reaction 1, the conversion of methane in this case being about 98 per cent. Values for the free energy and equilibrium constant calculated for Reaction 2 are as follows:

$T°$ K.	1,073	1,173	1,273
ΔF	−11,251	−18,112	−24,943
K_p	194.8	2.353×10^3	1.899×10^4

Aliphatic hydrocarbons of higher molecular weight are more easily and more rapidly decomposed by these reactions than is methane; but their decomposition is complicated by the increasing ease with which heavier compounds crack to carbon and hydrogen, a fact which in itself seriously complicates the problem of recovery of all the carbon, besides rendering such processes unsuitable for the application of solid catalysts.

The methane-steam reaction has formed the subject of a number of patents (*2*, *7*). Those processes in which no catalyst is employed utilize the fact that at very high temperatures methane and steam react on practically any refractory surface, yielding carbon monoxide and hydrogen together with more or less free carbon. In most of those processes which employ catalysts, the entire converter chamber is heated externally by some means, and a methane-steam mixture is passed through in a continuous stream.

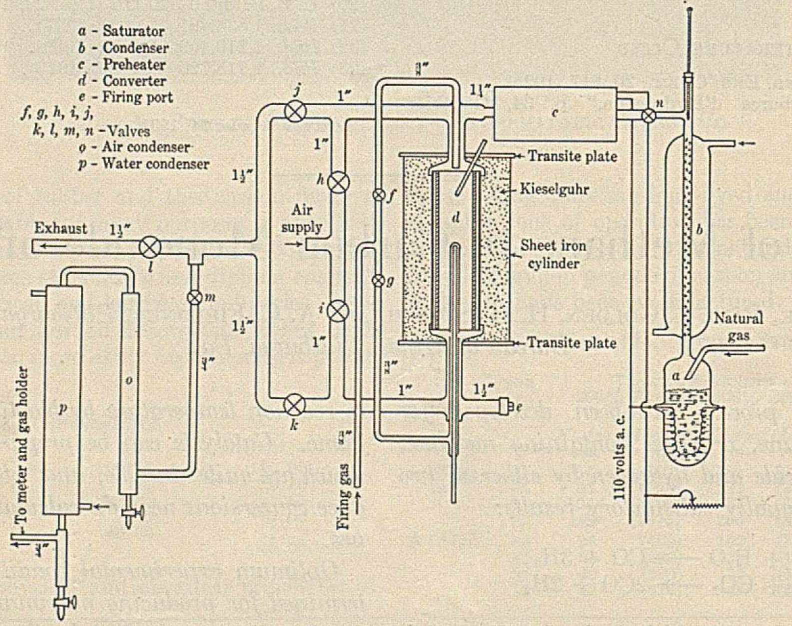

Figure 1. Apparatus for Conversion of Methane to Carbon Monoxide and Hydrogen

Fischer and Tropsch (*4*) investigated the effect of a large number of catalysts on these reactions, and their publication contains the most complete general information available on the characteristics of the process. Working at temperatures between 860° and 1000° C., they reported high conversions on metallic catalysts at high gas velocities in a small externally heated laboratory apparatus, using either carbon dioxide or steam with methane. Experiments in which the gas mixture was passed over hot coke did not result in such good conversions. They reported that their best metallic catalysts, composed of cobalt or nickel, and promoted with aluminum oxide and carried on a refractory supporting material, were not seriously injured by the presence of sulfur compounds in the original gases. They found that the initial conversions were higher than those obtained after their catalysts had been in use for some time, but that this loss of activity soon ceased (ostensibly when the catalysts had become saturated with sulfur) and was succeeded by an apparently constant state of activity for an indefinite period. They do not report the presence of free carbon or other products of side reactions.

A detailed report of both small-scale and pilot-plant investigations on the catalytic hydrolysis of methane has been recently published by Gluud, Klempt, Brodkorb et al. (*5*). This work indicates that external firing may be employed, a satisfactory heat-resistant material for the construction of the reaction vessel being an alloy containing 20 per cent nickel, 25 per cent chromium, and 55 per cent iron. The experiments were, however, mainly concerned with the production of a nitrogen-hydrogen mixture by the use of air, steam, and methane as raw materials. The heat-transfer problem is, of course, much simpler where some air is mixed with the methane and steam, the endothermic hydrolysis of methane being thus partially counterbalanced by the exothermic combustion of methane.

The difficulties involved in externally heating large catalytic units for this process, in which the heat quantity required is very great owing to the endothermicity of the reactions, make it quite desirable to effect the heat transfer by internal heating if possible. With this in view, it was decided to carry out the present investigation in an apparatus in which the heat of reaction was supplied to the gases by the catalyst bed, heated to reaction temperature by direct blasting with a gas-air mixture. It was found that satisfactory catalysts could be prepared which were uninjured by this method of heating, even when the gas was burned in a moderate excess of oxygen on the catalytic surface. This permitted the development of a cyclic process for converting methane, similar in operation to the blue-water gas process.

Apparatus Used

Figure 1 shows the apparatus. The working parts, with the exception of the saturator which is made of glass, are constructed of standard pipe and pipe fittings. All removable connections subjected to high temperatures are lubricated and made gas-tight with a paste of powdered graphite and linseed oil. The only unit parts deserving special comment are the converter and saturator. The converter chamber is shown in detail in Figure 2, and consists essentially of a section of 4-inch (10.2-cm.) iron pipe, 20.5 inches (52 cm.) long, inside of which an alundum tube of the same length and 3 inches (7.6 cm.) inside diameter is cemented with a mixture of kieselguhr and sodium silicate. This refractory lining serves to protect the iron casing from the influence of gases containing free oxygen and carbon at high temperatures, which would otherwise quickly convert it to a quite useless condition, besides contaminating the catalysts with iron. The entire converter unit is contained in a sheet-iron cylinder and insulated with dry packed kieselguhr. It is so constructed that it is easily separated from the rest of the line by removing appropriate pipe connections at the ends, thus facilitating emptying and recharging. A platinum-platinum-rhodium thermocouple is used to measure the temperature at the top of the catalyst bed; a compound two-junction couple of the same material is used for the center and bottom. The junctions of the top and bottom couples are, respectively, equidistant from the top and bottom of the catalyst bed.

Water vapor is introduced with methane into the converter in predetermined ratio by saturation at some definite temperature. This is accomplished in the saturator system as follows:

> The water in the saturator can be vaporized at any desired rate by adjustment of the energy consumption of the heating coil immersed in the water. Gas passing through the saturator

carries with it water in amounts dependent on the rate of the forced vaporization, this rate being so adjusted that the quantity of water introduced is in excess of that required by the experiment. The gas-steam mixture then passes into the condenser tube, which contains a long roll of tightly rolled copper gauze. This serves to break up the direction of gas flow, facilitating condensation of excess water and helping to equalize the final temperature of the gas. The apparatus is so adjusted that water vapor continuously condenses throughout the length of the tube, and, as the gas is always in contact with liquid water, the mixture leaving the side tube at the top consists of gas saturated with water at the temperature recorded at this point. Experience has shown that this method of saturation, when carefully controlled, will yield fairly duplicable results at temperatures as high as 87° C. The actual amount of water introduced was determined, when balance-sheet data were desired, by actual weight measurement; otherwise it was calculated from the combined oxygen in the carbon monoxide, carbon dioxide, and unchanged water in the exit gases. This method of calculation gives values of the steam concentration which are accurate to ±2 per cent.

A complete operating cycle is as follows:

The catalyst is heated to reaction temperature by blasting with a gas-air mixture, the direction of firing being periodically reversed by the reversing valve systems $f-h-k$ and $g-i-j$ until the entire mass is heated to a sufficiently uniform temperature. The gas-air supply is then shut off, and the apparatus purged of products of combustion by introducing steam and gas through an auxiliary saturating system, allowing the reaction products of this operation to flow to the atmosphere. Connections to the exit meter and gas holder are then opened, and a gas-steam mixture blown through until the lower thermocouple records a temperature too low for the purposes of the experiment. As the direction of the gas-steam flow is not reversed, the temperature at the top and middle of the converter falls very rapidly, so that the reaction zone at the end of a "make" period is not more than one-fourth as large as at the beginning. The heating cycle is then repeated, and so on. Provision is made to measure the excess water condensed from the exit gases in the air and water condensers, and the gas formed during the experiment is subsequently analyzed.

PREPARATION OF CATALYSTS

The catalysts were prepared by evaporating solutions of metallic nitrates to dryness in contact with sized pieces of porous highly refractory material. In this manner the pores of the refractory were filled with the salt, which was then more or less completely decomposed to the oxide by heating to 250–300° C. for several hours in an electric oven. The individual pieces of refractory were approximately 3 mesh. Two liters of such pieces constituted one charge of the converter.

Reduction to the metallic state was accomplished after the catalyst had been placed in the converter. The method was simple, consisting merely of burning natural gas in contact with the catalyst in a supply of air insufficient to produce carbon dioxide and water, thereby furnishing a reducing atmosphere. From room temperature to 700° C. the heating and reduction were effected slowly by careful regulation of the heating mixture; above 700° C. it was allowed to proceed more rapidly, the final temperature of reduction being 1050° to 1150° C. The entire process was usually completed in 4 to 4.5 hours.

The results to be discussed later do not include a study of the effect of time and temperature of reduction on catalytic activity, owing to the obvious difficulties involved in such a series of experiments in which this method of heating is employed.

INDIVIDUAL CATALYSTS. One-half pound (0.23 kg.) of nickel nitrate (as $Ni(NO_3)_2 \cdot 6H_2O$) was dissolved in a small amount of water, and the salt deposited on pieces of burned corundite (a commercial refractory high in Al_2O_3) by evaporation. Ignition and reduction were accomplished by the method just described.

One pound (0.45 kg.) of nickel nitrate on burned corundite.

Two pounds (0.9 kg.) of nickel nitrate on burned corundite.

One pound (0.45 kg.) of cobalt nitrate (as $Co(NO_3)_2 \cdot 6H_2O$) on unburned corundite.

One pound (0.45 kg.) of nickel nitrate and 2.6 (1.17 kg.) of aluminum nitrate (as $Al(NO_3)_3 \cdot 9H_2O$) on unburned corundite. The atomic ratio of nickel to aluminum was 1:2.

Nickel and aluminum nitrates on unburned corundite. The atomic proportions of nickel to aluminum were 1:1.

One pound (0.45 kg.) of nickel nitrate on unburned corundite.

One pound (0.45 kg.) of nickel nitrate on burned alundum.

EXPERIMENTAL RESULTS

Because the method of supplying heat for the reaction prevented the maintenance of either a constant temperature or a uniform rate of change of temperature throughout the catalyst, it was impossible to make a study of the effect of temperature on the characteristics of the process. For this reason the same approximate range was selected for all experiments, the mean temperature in this range being considerably higher than the minimum acceptable value of 900° C. This inflexibility narrowed the scope of the investigation to a study of the most favorable experimental conditions for obtaining uniformly high conversions in the standard temperature range. It was found that the nature of the reactions involved simplified this phase of the problem very considerably and permitted the standardization of experimental conditions, so that the greater part of the data to be presented represents the best results to be expected from the various catalysts under the operating conditions adopted for this work.

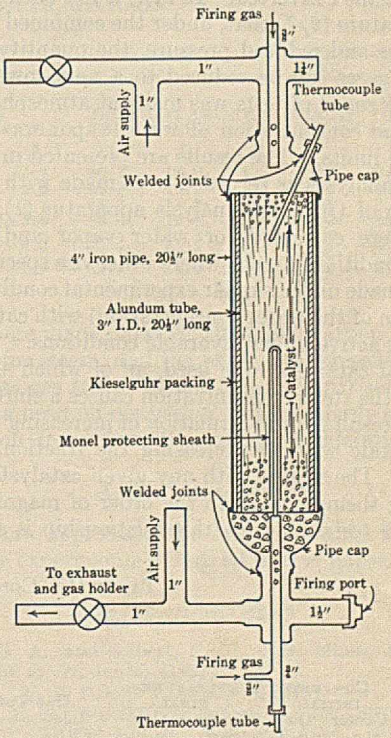

FIGURE 2. DETAILS OF CONVERTER

The most important feature was the necessity for obtaining stable catalysts. As previously stated, the best catalysts were found to be mechanically and chemically sturdy to the damaging influence of high temperature. Pittsburgh natural gas was used as raw material throughout the investigation. Its sulfur content is very low, hence the susceptibility of the catalysts to the poisoning influence of sulfur compounds is unknown. It is very probable, however, in view of Fischer's results, that, even when this element is present in relatively

TABLE I. EFFECT OF WATER CONCENTRATION ON NATURE OF REACTION PRODUCTS

TEST	CATALYST	CONVERTER TEMPERATURE INITIAL Center	INITIAL Out	FINAL Center	FINAL Out	GAS VOLUME Inlet[a]	GAS VOLUME Exit	CO_2	EXIT-GAS ANALYSIS H_2	CO	CH_4	INLET-GAS ANALYSIS CH_4	C_2H_6	N_2	NATURAL GAS DECOMPOSED	WATER CONCN. IN ENTERING GAS
		° C.	° C.	° C.	° C.	Liters	Liters	%	%	%	%	%	%	%	%	%
19	2	1055	1235	915	1035	56.7[b]	220[b]	0.8	71.2	23.7	1.5	80.9	17.2	1.9	94.0	54
18	2	1115	1115	995	1065	56.7[b]	225[b]	0.9	69.7	25.0	1.3	80.9	17.2	1.9	95.0	57
20	2	1085	1265	910	1050	56.7[b]	228[b]	2.0	72.1	23.0	1.4	80.9	17.2	1.9	94.5	60
30	5	1070	1065	800	820	98.9	363	0.9	70.8	23.3	3.9	80.2	17.6	2.2	85.7	53
31	5	1070	1070	735	910	81.6	314	2.4	72.0	21.7	3.1	80.2	17.6	2.2	88.2	58
29	5	1025	1070	750	910	66.9	273	3.5	69.6	20.2	3.1	80.2	17.6	2.2	87.3	65
46	8	1135	1020	805	875	101.7	405	1.6	71.6	23.7	1.7	83.9	14.9	1.2	93.3	56
47	8	1130	945	800	830	91.5	361	5.0	71.7	18.8	3.2	83.9	14.9	1.2	87.3	69

[a] The values for inlet-gas volumes in this and the following tables do not include steam volumes.
[b] Gas volumes not corrected to standard conditions.

large quantities in the reactant gases, it will be largely converted to hydrogen sulfide and pass into the exit gases without seriously injuring the catalysts.

In considering the properties of the reaction

$$CH_4 + H_2O \longrightarrow CO + 3H_2$$

it is at once evident at any given pressure that, exclusive of the possibility of changing the velocities of side reactions, an excess of water in the reactants favors an increase in the fraction of methane converted. In fact, it has been stated in the patent literature (*2*, *7*) that, under the combined influences of excess water and reduced pressure, the quantity of methane in the exit gases can be reduced to a very low figure. Accordingly, a series of tests was made at atmospheric pressure in which the concentration of water vapor was varied over rather wide limits. The results are presented in Table I.

The gas analyses as recorded were made with a Bureau of Mines type of Orsat gas-analysis apparatus (*1*), and all gas volumes were corrected for water vapor and reduced to standard conditions except where otherwise specified. These tests were made under similar experimental conditions (expect for variation of the water concentration) with catalysts which were highly active under favorable conditions. Three different types of catalysts were used, all of which show that an increase in the steam concentration causes a shift in the reaction which results in the formation of increasing quantities of carbon dioxide without increasing the fraction of methane converted. The results with any given catalyst agree fairly well among themselves as to the order of magnitude of this effect. The tests in which this relationship is shown to the best advantage are 46 and 47, in which it was possible to make very satisfactory balance sheets. In test 46 the volumetric relations of natural gas to steam were 1:1.27, and in test 47 they were 1:2.2. The data from these tests show that an increase in the partial pressure of water in the reactants is followed by an increase in the carbon dioxide content of the products. At the same time there is an apparent decrease of the total methane converted under these conditions. A consideration of the possible reactions by which carbon dioxide may be formed shows that in the presence of an excess of water vapor two consecutive reactions may occur in the following order:

$$CH_4 + H_2O \longrightarrow CO + 3H_2 \tag{1}$$
$$CO + H_2O \longrightarrow CO_2 + H_2 \tag{3}$$

The relative velocities of these two reactions in the hot zone, as well as the shift in the equilibrium of Reaction 3 upon passing through the temperature gradient at the exit of the reaction vessel, are important factors in determining the amount of carbon dioxide present. The most favorable conditions for the hydrolysis of methane to carbon monoxide and hydrogen are, however, obtained when the composition of the reactant mixture is that required by Reaction 1.

The decreased conversion of hydrocarbons observed in those tests in which the water concentration in the reactants was high may be due to a decreased time of contact. For example, in tests 46 and 47 the rate of input of natural gas was very nearly the same in both cases, but in test 46 the steam concentration was 56 per cent, and in test 47 it was 69 per cent. This means that in the latter case the total space velocity of the reactants (steam plus gas) was about 1.4 times greater; or the time of contact in test 46 was about 40 per cent longer.

The results of representative tests on several catalysts are presented in Table II.

TABLE II. CONVERSION OF NATURAL GAS–STEAM MIXTURES

(Comparative tests on catalysts)

TEST	CATALYST	CONVERTER TEMPERATURE INITIAL Center	INITIAL Out	FINAL Center	FINAL Out	GAS VOLUME Inlet	GAS VOLUME Exit	CO_2	EXIT-GAS ANALYSIS H_2	CO	CH_4	INLET-GAS ANALYSIS CH_4	C_2H_6	N_2	SPACE VELOCITY OF INLET GAS[a]	NATURAL GAS DECOMPOSED	WATER CONCN. IN INLET GAS
		° C.	° C.	° C.	° C.	Liters	Liters	%	%	%	%	%	%	%		%	%
8	1	1145	...	960	...	70.8[b]	202.0[b]	2.5	71.1	22.0	4.3	...	...	...	362	88.0	..
18	2	1115	1115	995	1065	56.7[b]	225.3[b]	0.9	69.7	25.0	1.3	80.9	17.2	1.9	400	95.0	57
19	2	1055	1235	915	1035	56.7[b]	219.5[b]	0.8	71.2	23.7	1.5	80.9	17.2	1.9	488	94.0	54
37	3	1140	1100	1005	1045	868	3114	2.6	68.7	26.1	0.8	80.9	17.2	1.9	301	97.1	60
22	4	1080	1230	955	980	147.8	474	1.9	63.8	21.3	9.7	80.9	17.2	1.9	246	69.0	58
24	4	1190	1160	960	980	49.8	113.9	1.6	48.7	15.7	30.1	80.9	17.2	1.9	284	31.3	53
27	5	1060	1030	810	910	124.6	486	2.4	67.4	21.0	3.0	80.2	17.6	2.2	197	88.4	58
31	5	1070	1070	735	910	81.6	314	2.4	72.0	21.7	3.1	80.2	17.6	2.2	262	88.2	58
33	5	1075	1080	745	920	73.6	279.5	1.8	69.7	21.2	5.1	80.2	17.6	2.2	333	80.8	55
38	7	1100	1115	780	975	710	2888	1.4	70.9	23.9	1.4	85.7	13.0	1.3	425	94.3	57
43	8	1075	1035	740	830	398	1631	1.2	71.1	23.5	2.2	88.4	10.8	0.8	396	91.0	57

[a] Space velocity = ratio of volume of reactants passed through converter per hour to volume occupied by catalyst.
[b] Gas volumes not corrected to standard conditions.

A brief survey of these data discloses the fact that catalysts prepared from nickel nitrate and a refractory supporting material gave the most consistently high conversions. For example, catalysts 1, 2, 3, 7, and 8, used respectively in tests 8, 19, 37, 38, and 43, were prepared from nickel nitrate and corundite or alundum, and produced high conversions not far below the calculated equilibrium values. Practically no free carbon appeared in the reaction products. It should also be pointed out that the proportions of nickel to refractory were varied quite considerably in this series of preparations which would permit the preparation of large quantities of satisfactory catalyst more cheaply than apparently is indicated by the proportions in most of those used in this investigation.

It is shown later that these catalysts are also quite durable. The activities of the members of this particular series were not at all affected by the differences in the chemical constitution of the supporting materials used. The explanation of this experimental fact was found by an examination of their physical state after more or less extended use. The individual particles had suffered no disintegration from being subjected to high temperatures; and the surface of each was found to be completely covered with a shining layer of metallic nickel. This metallic film adhered to the refractory so tenaciously as to leave the impression that it had been placed there by fusion. The characteristics of this metallic film indicate that in such catalysts the active surface is composed of metallic nickel, and that any promoter effect of the carrier is only of secondary importance, if of any importance at all. It is undoubtedly true that these catalysts owe their physical stability largely to the properties of the supporting material but it is also evident that this effect is to be attributed to the ability of the carrier to withstand distintegration at high temperature.

Cobalt catalysts (tests 22 and 24) were entirely unsatisfactory in every respect.

Two catalysts of the type found most satisfactory were subjected to durability tests, the results of which are presented in Table III.

Tests 38, 39, and 40 were made with a nickel-corundite catalyst over a period of several weeks. During the time interval between tests the catalyst was not in any way protected from oxidation by air at ordinary temperatures. These tests show that within the limits of error of the experiments there was no loss of activity. Tests 42, 43, and 46 were conducted in a similar manner with a nickel-alundum catalyst, which also completely retained its initial activity.

Little attention was devoted to the decomposition of methane by the reaction:

$$CH_4 + CO_2 \longrightarrow 2CO + 2H_2$$

It has already been shown that this reaction would be expected to proceed to approximately the same extent at temperatures between 800° and 1000° C. as the steam reaction. Two tests were made, however, in which carbon dioxide was substituted for steam, and the results are presented in Table IV. A steam-gas test is included for comparison.

TABLE III. CONVERSION OF NATURAL GAS-STEAM MIXTURES

(Durability tests on catalysts)

		Converter Temperature				Gas Volume		Exit-Gas Analysis				Inlet-Gas Analysis			Space Velocity of Inlet Gas	Natural Gas Decomposed	Water Concn. in Inlet Gas
		Initial		Final													
Test	Catalyst	Center	Out	Center	Out	Inlet	Exit	CO_2	H_2	CO	CH_4	CH_4	C_2H_6	N_2			
		° C.	° C.	° C.	° C.	*Liters*	*Liters*	%	%	%	%	%	%	%		%	%
38	7	1100	1115	780	975	710	2888	1.4	70.9	23.9	1.4	85.7	13.0	1.3	425	94.3	57
39	7	1085	1100	745	925	603	2428	1.3	71.8	24.1	2.0	85.7	13.0	1.3	421	92.0	57
40	7	1130	1065	775	880	486	2023	0.9	68.6	24.5	1.8	85.7	13.0	1.3	406	92.5	57
41	8	1070	1015	765	865	502	2060	1.4	70.0	23.6	2.9	88.4	10.8	0.8	397	88.1	57
42	8	1090	1070	765	850	463	1960	1.2	71.8	23.2	2.3	88.4	10.8	0.8	409	90.5	57
43	8	1075	1035	740	830	398	1631	1.2	71.1	23.5	2.2	88.4	10.8	0.8	396	91.0	57
46	8	1135	1020	805	875	101.7	405	1.6	71.6	23.7	1.7	83.9	14.9	1.2	453	93.3	56

Catalysts prepared from nickel and aluminum nitrates were not sufficiently stable to be of value. The results of tests 27, 31, and 33 plainly show this fact. A catalyst, similar to the one used in these three tests but containing a larger proportion of nickel, was highly active at first, comparing favorably with nickel catalysts; but its loss of activity was so rapid and complete that no results are recorded. When the reduced nickel-alumina catalysts were examined, the surface of each particle of refractory was found to be covered with an easily removable gray film of finely divided material. It seems probable that the rapidity with which these contact materials lost their activity may have been largely due to the ease with which the active nickel, or mixture of nickel and aluminum oxide, may have been removed from the refractory surface by the mechanical action of gases passing over it at high velocity.

TABLE IV. CONVERSION OF NATURAL GAS-CARBON DIOXIDE MIXTURES

	Test		
	44	45	43
Catalyst	8	8	8
Converter temperature, ° C.:			
Initial:			
Center	1090	1105	1075
Out	1045	1035	1035
Final:			
Center	785	790	740
Out	815	860	830
Inlet-gas volume, liters	463	506	398
Exit-gas volume, liters	1880	2082	1631
Exit-gas analysis:			
CO_2	3.8	3.5	1.2
H_2	45.8	46.0	71.1
CO	45.3	46.9	23.5
CH_4	3.5	2.2	2.2
Inlet-gas analysis:			
CH_4	88.4	88.4	88.4
C_2H_6	10.8	10.8	10.8
N_2	0.8	0.8	0.8
Space velocity, inlet gas	377	382	396
Natural gas decomposed, %	85.8	90.9	91.0
CO_2 in inlet gas, %	52	52	..
H_2O in inlet gas, %	..	..	57

These data need no discussion, as they merely substantiate the conclusion drawn from theoretical considerations.

ACKNOWLEDGMENT

The authors appreciate the help of David F. Smith in planning the experiments described in this paper.

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Experiments with a heat-treated copper-beryllium alloy containing about 2 per cent beryllium show that it compares favorably with good steel in tensile strength and hardness. It is said to possess high electrical conductivity, good casting qualities, and sonority. It is also reported to be satisfactory as to elasticity, resistance to fatigue, and non-corrosive properties. The development of this alloy follows several years' effort to produce beryllium commercially. The cost in the past two years has been reduced from $150 to $50 a pound.

Mechanical Handling in the Chemical Industry

E. J. Burnell

Link-Belt Company, Chicago, Ill.

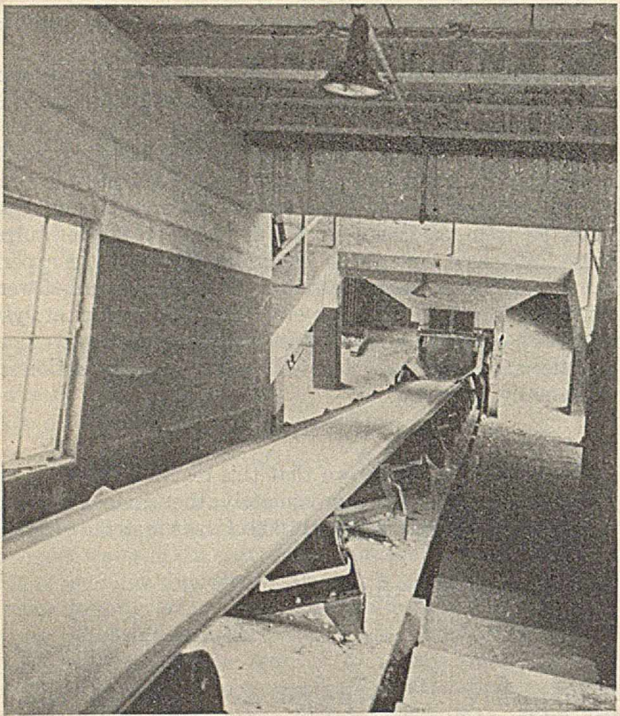


Figure 1. Belt Conveyor for Salt

MOVING materials from where they are to where they are wanted, or straight-line production, has been well developed in industry. Ideas and arrangements of conveyors in one industry have been adapted to problems in another industry, until today there is standardized equipment for nearly every job.

In the industrial plant where chemicals are handled, or in the chemical-preparation plant, there are many types of conveyors used to handle materials. Each type of the most popular conveyors and its function and application to the plant are subsequently described.

Belt Conveyors

The belt conveyor is especially well suited to the conveying of large quantities of bulk materials, such as sand, coal, ores, clay, and various chemicals. This type of conveyor operates at a low cost per ton, owing to its small power-consumption, and to the relatively large capacity that results from the continuous delivery of material at a specific belt speed.

The principal elements of this type of conveyor are the conveying belt covered with rubber or other material, the troughed multiroll idlers over which the belt moves on the carrying run, the straight rolls over which the belt returns on the bottom run, the end pulleys, and the driving machinery. Belt conveyors are installed horizontally or at inclinations up to 20°, or both horizontally and inclined; but it should be borne in mind that steep inclines are to be avoided, or the material will roll back and the belt carrying capacity be reduced. When the material must be elevated to a considerable height, the belt conveyor may be out of the question, because of insufficient space within which to make the grade.

The conveying belt may be from 12 to 60 inches wide, may operate at speeds up to 600 feet per minute (or faster), and may have its carrying-run supporting idlers spaced from 3 to 5 feet apart, depending upon the capacity required, the size of the lumps, and the weight of the material per cubic foot. The return idlers may be from 9 to 10 feet apart.

Today's idler is equipped with tapered roller bearings and with grease-seal reservoirs that need recharging only at very infrequent intervals by a grease gun. Attention necessary for maintenance is reduced to a minimum. Accurately made, well-balanced, well-lubricated, free-turning rolls result in long life of the equipment. Grease seals are important to keep the grease in the reservoir and to exclude dirt and grit from the moving parts.

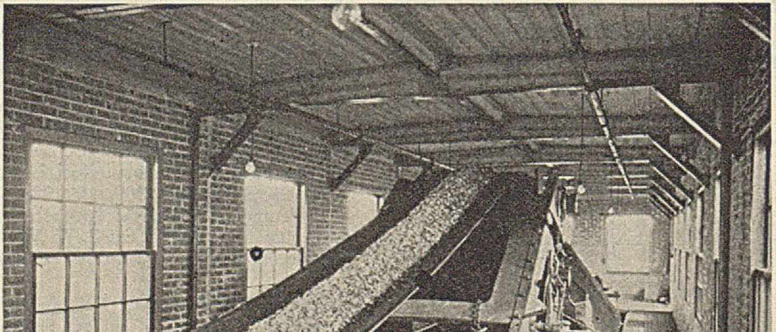


Figure 2. Belt Conveyor for Wood Chips

The belt-conveyor installation at plant of a rock-salt company, illustrated in Figure 1, shows a reciprocation feeder in the background delivering to a belt conveyor, 30 inches wide, running upward at a 20° angle. The idlers for this conveyor are granitized to prevent the salt from sticking to them.

The belt conveyor, 36 inches wide, shown in Figure 2, runs over the digester bins at the plant of a pulp and lumber company. This conveying unit distributes the wood chips to the digester bins. The chips are carefully screened before discharging to the belt-conveyor system, but this operation does not entirely remove all the sawdust; the remaining sawdust has a tendency to cling to the conveyor belt, and since it is desirable to remove all the sawdust from the chips before passing them on to the digester, it was necessary to provide a special belt-cleaning and collecting unit, mounted on the reversible traveling tripper. This outfit consists of a special cleaning brush and collecting screw conveyor, placed directly below the discharge pulley of the tripper. The screw conveyor collects and conveys the sawdust transversely to collecting hoppers.

There are additional uses for belt conveyors in handling of chemicals—for example, glass cullet or sand, lime, cement, or any bulk material.

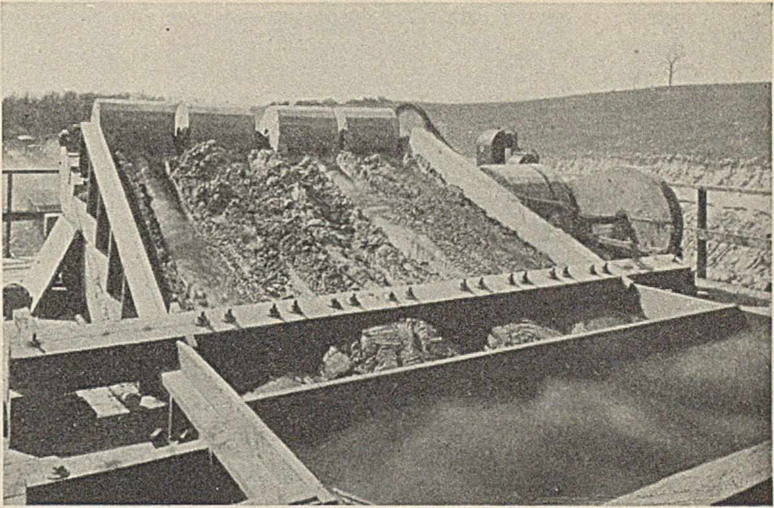


FIGURE 3. SCREW CONVEYOR FOR DEWATERING SAND

SCREW CONVEYOR

The screw conveyor is used to excellent advantage in the conveying of small-sized material in bulk, such as cement, grain, chemicals, sugar, or similar materials.

Screw conveyors are low in first cost, being exceedingly simple in construction and requiring very little head room. In fact, the screw conveyor can often be placed in close quarters where other forms of conveyors will not work efficiently. The conveying medium consists of a spiral mounted on a central shaft or pipe, and serves to push the material ahead in an all-steel or wooden steel-lined trough in which the spiral is rotated by suitable driving machinery. From the top of the conveyor trough the ends of the 8-, 10-, or 12-foot sections of standard screw conveyor are supported at intermediate points by means of hanger bearings.

The diameter of the conveyor or spiral may be as small as 3 inches and as large as 24 inches. The material is discharged either over the end of the conveying trough, or through gates fitted in the trough bottom where desired.

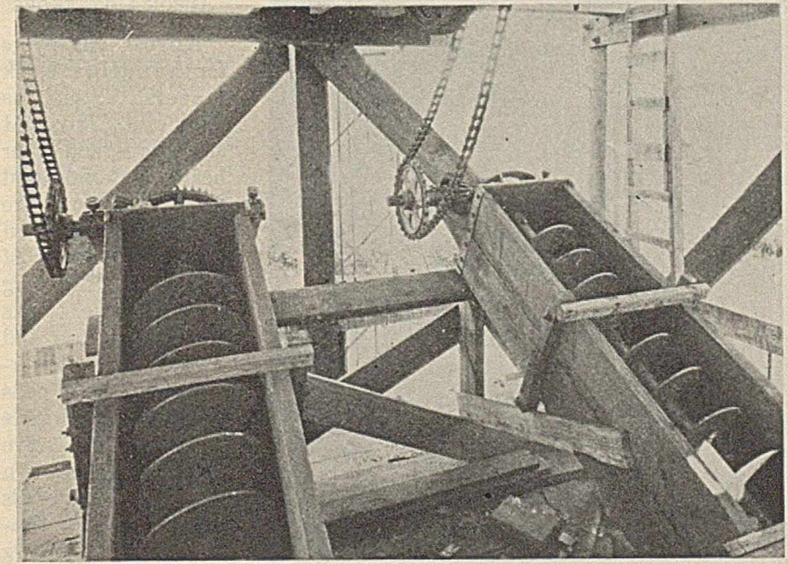


FIGURE 4. DEWATERING SCREW CONVEYOR

Sometimes there are several discharge openings with no gates, with the result that the material discharges through the first opening until the height of the pile reaches and closes the opening. The discharge will then be through the next opening in the trough, and so on, until the storage is full.

Screw conveyors are used for moving materials horizontally or at inclines not exceeding about 10°. As a rule, their use is confined to the lighter classes of service. When employed for conveying abrasive materials tending to cause rapid wear, the screw and trough should be constructed of cast iron, manganese steel, or heat-treated steel.

The screw conveyor is frequently used in sand and gravel washing plants as a dewatering device. The screw has a scrubbing action on the sand and keeps the loam and other foreign material in suspension, to be carried away in the overflow. Thus clean sand is secured for use where the specifications and inspections are rigid.

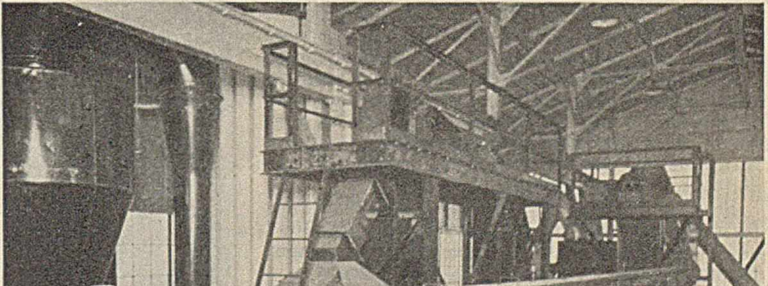
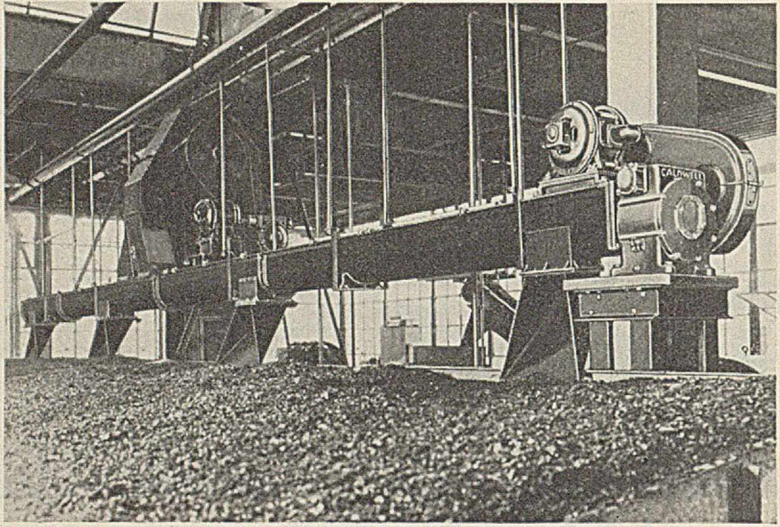
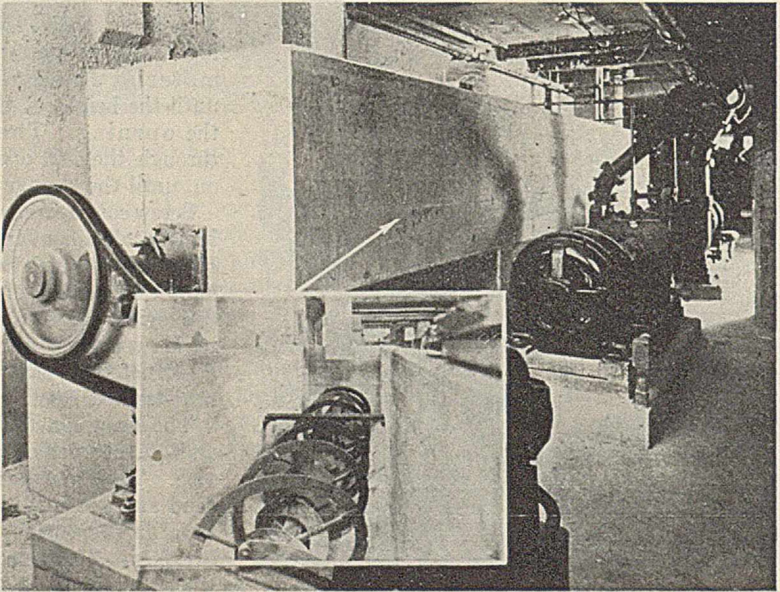


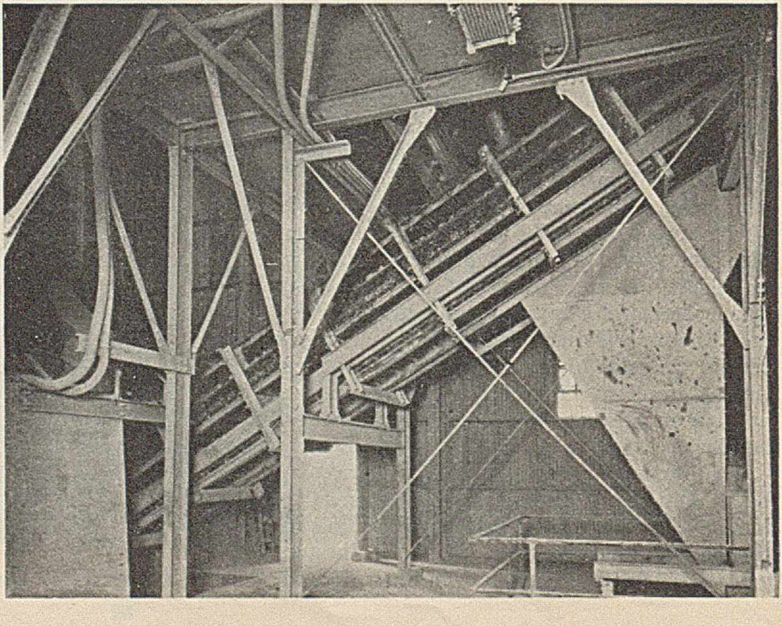
FIGURE 5. DISTRIBUTING SCREW CONVEYOR FOR RED LEAD



LEFT: FIGURE 6. SCREW CONVEYOR FOR SHREDDED RUBBER



CENTER: FIGURE 7. RIBBON SCREW CONVEYOR IN CEMENT PLANT



LOWER: FIGURE 8. APRON CONVEYOR FOR LIMESTONE

An example of this type of installation is shown in Figure 3. Four of these screws, 12 inches in diameter and 24 feet long, are shown in action dewatering sand. Another installation of these screws, showing their construction, is illustrated in Figure 4. These are typical examples of this use for screw conveyors.

In paint plants the screw conveyor has proven very satisfactory for handling batch material. Figure 5 shows a distributing conveyor, 6 inches in diameter, in a dust-sealed trough with special dust-tight discharge chutes, handling red lead from the elevator to the storage bins over the furnaces.

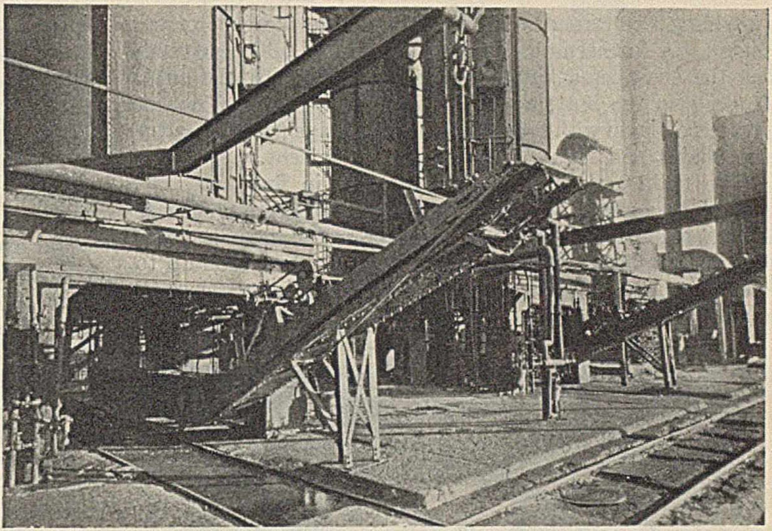
At the plant of a rubber company a screw conveyor is used for handling shredded rubber, and Figure 6 pictures how this is arranged to take care of a long storage pile. A screw conveyor drive with overhead motor mounting on a 9-inch helicoid conveyor is used for distributing the shredded rubber over drying racks. The special type of positive drive for this conveyor gives a positive, continuous flow of material at a predetermined speed. The elevator drive is shown in the background.

Screw conveyors are often used in special ways for mixing and agitating materials. Figure 7 shows the slurry agitator tank used at a cement plant; the insert pictures the ribbon screw conveyor used in the tank. Many similar installations are made in the chemical industry. Short sections are often used for stirring, such as on a cement mixer used in preparing mix for a concrete-block plant.

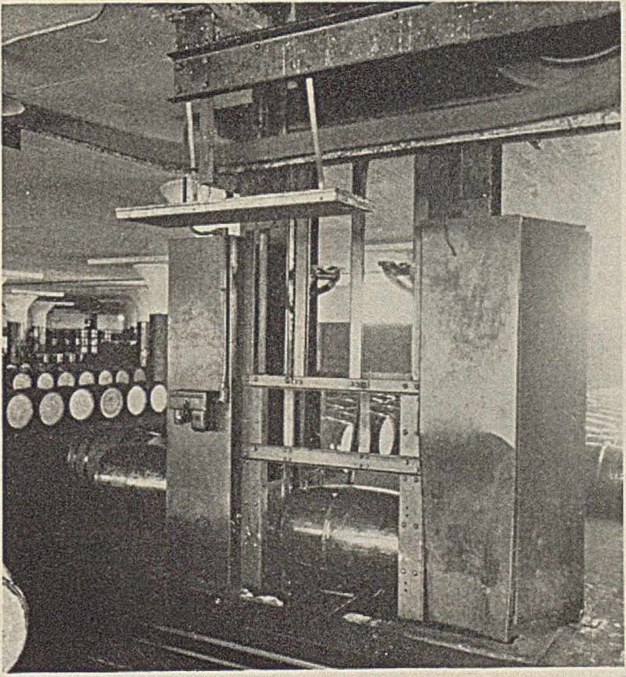
There are many applications of this type of conveyor that are in use, not only in the chemical industries, but in many varied industries. Cottonseed-oil mills and cotton gins are among the important users of this type of conveyor.

APRON CONVEYORS

Apron conveyors for handling bulk materials, such as coal, sand, crushed stone, ores, and other heavy materials used in production, are usually constructed with two strands of roller chain traveling on suitable tracks on both the top and bottom runs. Overlapping steel pans tie the two chains together and serve as the apron on which the materials are conveyed. Stationary retaining sides, or skirt boards, are used to permit



RIGHT: FIGURE 9. FLIGHT CONVEYORS FOR HOT REFINERY COKE



CENTER: FIGURE 10. DRAG CONVEYOR AND ELEVATOR FOR OIL DRUMS

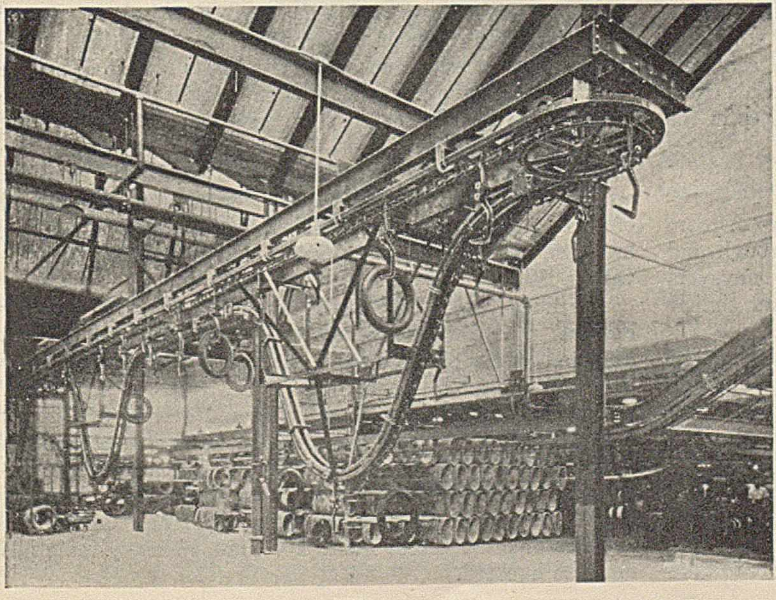
a greater depth of material to be carried.

Apron conveyors may be installed either horizontally, or at inclines up to about 25°. Owing to their substantial steel construction, the pans withstand the shock of dumping heavy masses of material upon them. As the conveyor operates at a slow speed, usually from 10 to 100 feet per minute, the maintenance cost is low.

The metal-mining field especially requires a heavy and very rugged and different type of apron feeder, as lumps up to 6 feet in dimension and weighing a ton or more are sometimes dropped in the pans from considerable height. To meet such conditions, the pans, chains, supporting rollers, and sprocket wheels, are all made of manganese steel and are of very rugged design.

The chains which operate this type of feeder are constructed so that they cannot articulate, bend, or sag below horizontal chain centers of the material-carrying run, but are free to flex in the opposite direction and bend around sprockets. The top-carrying run is the non-sagging portion of the feeder, and is the feature of this type of feeder.

One of the many typical examples of an apron-feeder installation is depicted in Figure 8. This steel apron feeder or conveyor, with width of 36 inches and pitch of 12 inches, handles limestone from the primary to the secondary crusher.



LOWER: FIGURE 11. TROLLEY CONVEYOR FOR TIRES

FLIGHT CONVEYORS

The flight or pusher type of conveyor was developed as a means of distributing non-abrasive materials horizontally, or elevating up to approximately 45°. The material is received in a trough, pushed along by flights attached to the chain at intervals, and usually discharged through openings in the bottom of the trough, being provided with gates to be opened or closed as the conditions require. In the early days the flight conveyor was made only with one strand of chain, the flight being fastened to it centrally, and was usually made of malleable iron with a thickened scraping edge, as well as with wearing pads for sliding the flights on steel tracks on the bottom run. In the flight conveyor the bottom run usually does the conveying.

The need for greater capacity was met by providing two strands of chain attached to the ends of the flights. A further improvement is the use of rollers suspending the chains and flights, instead of permitting the latter to drag on the bottom of the trough; the use of double strands of chain with rollers at the articulation points to carry the chains and flights is also an improvement.

The flight conveyor is not expensive in first cost, but should be avoided for handling abrasive materials, such as sand, etc., as the sliding or scraping action rapidly wears the trough lining. The conveyor operates at speeds up to 150 feet per minute, and is suitable for either lumpy or small materials.

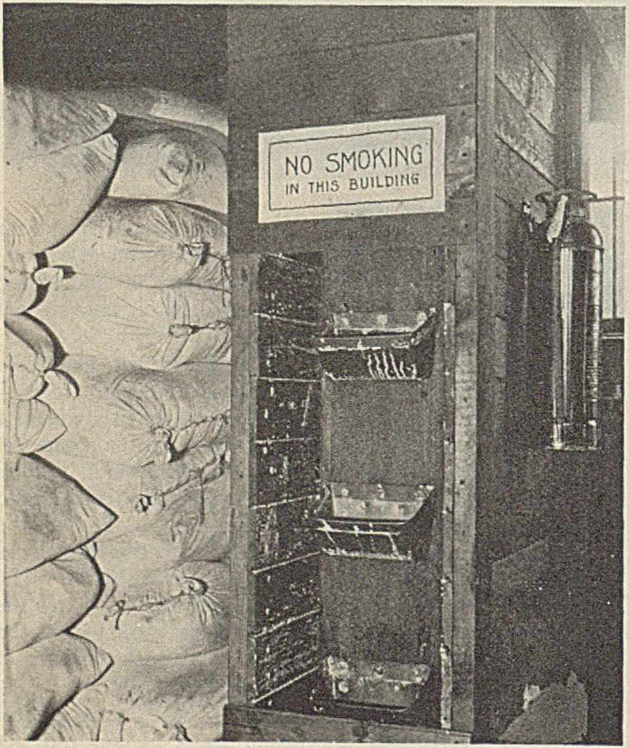


FIGURE 12. ELEVATOR CONVEYOR FOR SALT

The flight conveyors shown in Figure 9 are typical examples of the use of this particular conveying medium. It shows one of three batteries, of two flight conveyors each, for handling hot refinery coke from the stills to the quenching cars at the plant of an oil company. There are many other examples of this inexpensive but effective conveyor for handling lumpy chemicals, fertilizer-plant materials (such as charred bone), and even coal for the power house of the manufacturing plant.

DRAG CONVEYORS

Drag-chain conveyors are nothing more than two or more strands of chain of suitable type, sliding in a trough and carrying the material or package along. Such conveyors are used a great deal for conveying sawdust and similar materials.

The cast-steel drag chain is often used in conveying hot or cold cement clinker, a very abrasive product. This type of chain has broad wearing surfaces on the upper and lower sides. When worn on one side, the chain's usefulness can be renewed by turning it over in the trough and using the other side. The head of each link acts as a pusher for conveying the materials. Drag-chain conveyors should be operated slowly to keep the wear to a minimum.

Another type of drag conveyor is that using rollers to take the load from the chain links themselves, when being dragged through a trough. An example of this type of conveyor is depicted in Figure 10, showing the metal drums being conveyed in the plant of an eastern oil company.

Promal is especially suitable for conveyor use. A description of this chain occurs in a later paragraph.

OVERHEAD TROLLEY CONVEYORS

The overhead trolley conveyor saves floor space, makes ceilings or roof trusses pay dividends, and travels irregular paths as conditions may demand. This type of conveyor often turns obsolete plant layouts into straight-line methods without costly rebuilding. Its main features, besides flexibility, are low power consumption, initial cost, and maintenance.

A typical example of this type of conveyor (Figure 11) is the two-plane trolley conveyor for handling cured tires from the factory building to the warehouse of a tire and rubber company. This company uses this type of conveyor for handling parts and material going into the manufacture of tubes. Foundries use trolley conveyors for handling cores from maker through the ovens to the molder.

CHAINS AND BUCKET ELEVATORS

The centrifugal-discharge bucket elevator usually consists of malleable iron buckets spaced at intervals on a strand of chain, and operates at a speed of 200 to 300 feet per minute. The material is delivered into a boot, from which it is scooped up by the buckets, elevated, and discharged or thrown by centrifugal force, while passing over the head sprocket, into a chute usually leading to a bin or distributing conveyor. Although one of the earliest types, it is still an ideal bucket elevator for nominal capacity, for handling material that does not have very big lumps, and where operation is intermittent.

The perfect-discharge bucket elevator uses two strands of chain and has its bucket attached thereto at intervals. This type operates more slowly than the centrifugal type and has a pair of idler sprockets on the return side just below the head wheels to deflect the chains and completely invert the buckets, thereby effecting a perfect discharge. Because of the slower pick-up and discharge, the perfect-discharge elevator results in less breakage of friable lumps in the material elevated. When used on an incline, the deflector sprocket may be omitted.

The continuous-bucket elevator is made with steel buckets fastened continuously and very close together on one or two strands of chain or on a rubber or canvas belt. The flanged front of each bucket forms a chute for the discharge from the succeeding bucket, thus effecting a clean discharge at slow speed. This slow speed, with the use of a loading leg, permits the feeding of the material directly into the buckets, avoiding the wear and strain of digging through an accumulation of crushed stone, ore, or other material of a bulky or gritty nature in an elevator boot, thus reducing breakage of the material elevated and prolonging the elevator's life.

The bucket speed is usually about 100 to 150 feet per minute. The continuous-bucket elevator has a greater first cost than either of the others, but it has a greater capacity at a slower speed. More buckets are required than with the two former types, and the chain and driving machinery must be heavier to carry the greater load and to handle the same quantity in a given time. The continuous bucket-elevator was developed to fill the need for a better elevating unit than the centrifugal-discharge type, and is used in quarries or other places where a volume of heavy materials must be handled.

A typical elevator installation is shown in Figure 12; the 10 × 6 inch monel-metal buckets on a belt elevator are used for handling salt at a western salt plant.

Promal chain, which is especially suitable for conveyor use, was developed by the Link-Belt Company of Indianapolis and for the past four years has proved a very superior metal for chains. Promal is a specially processed malleable iron, the process employed transforming it into a material of radically different microstructure and physical properties. This metal has many excellent characteristics which make it extremely satisfactory for use where cast chains are used on conveyors, or elevators where abrasive materials are contacted. Cement mills, fertilizer plants, chemical plants, sand and gravel plants, and coal mines, as well as pulp and paper mills, have been the proving ground for chains made of Promal. Everyone of them has obtained from one and a half to five times the wear from Promal chains that they have from chains made from the best available iron.

Some of the physical properties of this metal are:

Yield point, lbs./sq. in.	50,000
Ultimate strength, lbs./sq. in.	70,000
Fatigue strength, lbs./sq. in.	33,000
Elongation, % in 2 inches	10 to 14
Modulus of elasticity	26,000,000
Coefficient of thermal expansion, inch	0.0000109
Specific gravity	7.35
Average Brinell hardness	170 to 190

CONCLUSION

While only touching upon the wide field of application and citing few specific examples of installations in the chemical industry, some idea is given of the extent to which mechanical handling enters into the expediting of deliveries, enlarging handling capacities, and reducing production costs.

Good engineering must extend to every detail of a conveying system, and must especially consider the nature and size of the material to be handled, whether it is sticky or abrasive, and the manner in which the material is to be fed to and discharged from the system.

RECEIVED August 11, 1931.

Power and Fuel Gas from Distillery Wastes

C. S. BORUFF AND A. M. BUSWELL, *State Water Survey, Urbana, Ill.*

HOT DISTILLERY wastes containing 3 to 4 per cent solids and 0.2 per cent organic acids may be fermented thermophilically to produce fuel gas (a mixture of methane and carbon dioxide) at very low cost. From an average daily volume of 1,500,000 gallons of this waste, 3,600,000 cubic feet of gas could be produced. A gasification of 58 to 72 per cent of the organic matter is accomplished in 2 to 6 days.

A stable inoffensive sludge (residue) is formed, as well as a liquor that can safely be drawn to sewers.

DISTILLERY wastes in the main always have been a liability. Methods of salvaging them for use as stock food or fertilizer base have been investigated and some are used by distilleries today. Methods of recovering the organic acids and glycerol have also been studied. The use of this material as a binder for fuels and for other purposes (*9*) has also been proposed. None of these procedures, however, has netted a substantial profit.

The sanitary disposal of beer-slop wastes is a serious problem. Usually they are about 20 times as heavy as normal sewage and contain a very high percentage of organic matter. The literature indicates that treatment plants handling sewage which contains a moderate amount of this waste will operate with difficulty (*6*).

Danok (*3*) suggested a pure culture method of decomposing such wastes. He states that the success of his method depends on the use of a sterile waste and a pure culture of specific bacteria. A British patent (*1*) outlines a process for the aerobic or anaerobic decomposition of such wastes by the addition of "betaine-destroying organisms." Neave and Buswell (*7*), in 1928, reported studies on the anaerobic stabilization of slops from an alcohol plant. In their batch experiments they found that slop diluted 1 to 4 still inhibited bacterial growth, but that when it was diluted 1 to 9 with sewage and inoculated with sewage sludge it fermented smoothly at 77–81° F. (25–27° C.), with the formation of carbon dioxide and methane, but with the destruction of only 55 to 65 per cent of the solids in 73 days.

Hatfield (*4*), after studying the rate of settling and gasification of Commercial Solvent beer-slop waste, reported that when diluted with 6 to 13 parts of sewage the solids were easily settled out. He found that the sludge was readily digested with sewage solids and that it produced the same quality and quantity of gas as the organic matter from sewage.

The settling of beer-slop waste with sewage, however, removes only about 30 per cent of the total waste load, leaving the rest to be handled by activated sludge or trickling filter units. The supernatant liquor from a settling tank being treated with 1 volume of beer-slop to every 9 volumes of average sewage would still be 2 to 3 times as strong as average settled sewage. This would place an excessive load on the activated sludge or trickling filter units. "The cost of treating such a strong waste," Hatfield says, "makes its recovery as a by-product within the industry necessary and advisable." At the time of Hatfield's studies the Commercial Solvent Corporation was fermenting corn mash. The residue from this fermentation (1,250,000 gallons a day) had a total solids content of 11,196 p. p. m. Hatfield calculated the population equivalent of these wastes to be about 800,000. Since that time the Commercial Solvents Corporation has used rye and the solids content of its waste has been materially increased.

GAS YIELDS FROM FERMENTED WASTES

On the basis of related studies (*2*) by the writers, it was thought advisable to see what gas yields could be obtained by the fermentation of the undiluted Commercial Solvent waste. As the temperature of the raw waste ran from 194° to 203° F. (90° to 95° C.), it was decided to try a thermophilic digestion. Such fermentations have long been recognized as much more rapid than those conducted at ordinary mesophilic temperatures. Table I gives an analysis of the waste used in this investigation. About half the solids were found to be filterable. This waste is much heavier than that used in the mesophilic studies by Neave and Buswell (*7*) and by Hatfield (*4*).

Anaerobic fermentation tanks (1 to 2 gallon capacity) were constructed with tubes for feeding and withdrawing liquor, residue, and gas. The gas was collected in gasometers and analyzed frequently. These fermentation tanks were started by adding liquor and sludge from a thermophilic tank in which an active culture of gasifiers had been developed. All tanks were operated at 127° F. (53° C.). The fermentation tanks, after they were well started, were fed at different rates. For example, one tank was fed at the rate of one-half its volume of waste per day (tank volume = twice the volume of waste), and another at the rate of one-third its volume of waste per day (tank volume = 3 times volume of waste). These experiments extended over seven months. The first three months were devoted to a determination of the rate at which the sour slop liquor could be fed to the fermentation vessels without inhibiting the bacterial action. The data submitted were obtained from a subsequent uninterrupted 4-month run.

TABLE I. ANALYSIS OF COMMERCIAL SOLVENT BEER-SLOP WASTE

pH	4.5–5.3
Total solids, p. p. m.	28,000–40,000
Volatile matter, p. p. m.	26,000–36,000
Volatile acids (as acetic), p. p. m.	1,800–2,400
Ammonia nitrogen, p. p. m.	14–86
Total nitrogen, p. p. m.	1,400–1,900
B. O. D., 5-day, p. p. m.	17,000
Oxygen consumed, p. p. m.	10,000–20,000
Temperature of waste as drawn, ° F.	194–203
Total solids:	
Ash, %	10
Protein (org. N × 6.25), %	32
Fats and oils, %	8
Total carbohydrates (less cellulose) as glucose, %	21
Undetermined (crude fiber, etc.), %	29

Figure 1 and Table II summarize the gas data. By feeding slops at the rate of 1 volume a day to a tank of twice this volume, 14 volumes of gas per volume of slop, in other words, 7 volumes of gas per unit of tank volume, can be obtained daily. If, on the other hand, the tank has a 4-volume capacity, giving the waste a longer detention period, 16.8 volumes of gas may be recovered each day from 1 volume of waste fed. If the same volume of waste is fed each day to a tank 6 times this volume, giving the waste a detention period of 6 days, 18 volumes of gas, or 3 times the fermentation tank volume per day, can be recovered. The gas recoveries for the different tank volume to waste volume ratios are given in Table II.

TABLE II. GAS PRODUCTION DATA AND RELATED CALCULATIONS

TANK VOLUME	YIELD OF GAS (Volumes per Tank Volume per Day)	ANALYSIS OF GAS[a] CH$_4$	ANALYSIS OF GAS[a] CO$_2$	ANALYSIS OF GAS[a] B. t. u.	INTEREST,[b] AMORTIZATION AND REPAIR CHARGES PER 1000 CU. FT. GAS	CHARACTER OF RESIDUAL WASTE
Times volume of waste		%	%		*Cents*	
2	7.0	55	43	550	2.34	Sludge fairly stable; overflow liquor unstable[c]
3	5.2	..	..	...	3.15	Liquor unstable[d]
4	4.2	58	40	580	3.90	Liquor unstable[e]
6	3.0	58	40	580	5.46	Liquor fairly stable, but contains only 10 per cent of original solids;[f] sludge stable

[a] Contains 0.1 to 0.5 per cent H_2 and 1 to 3 per cent N_2.
[b] Figured at 12 per cent on the investment.
[c] Organic matter gasified = 58% total added.
[d] Organic matter gasified = 63% total added.
[e] Organic matter gasified = 67% total added.
[f] Organic matter gasified = 72% total added.

Heukelekian and Rudolfs (*5*) reported that they can feed thermophilic sewage digestion tanks at a rate as high as 77 pounds of volatile matter per day per 1000 cubic feet of tank capacity (23.5 grams per day per 19-liter tank). From this digestion they were able to recover 1.2 volumes of gas per tank volume per day (Table III). This has been considered a very rapid digestion. The writers have been able to feed 930 pounds of volatile matter per day per 1000 cubic feet of tank capacity and to recover 7 volumes of gas per unit of tank volume per day. With the lower rate of feeding, whereby the waste is more thoroughly stabilized, an average of 3 volumes of gas per unit of tank volume can be recovered.

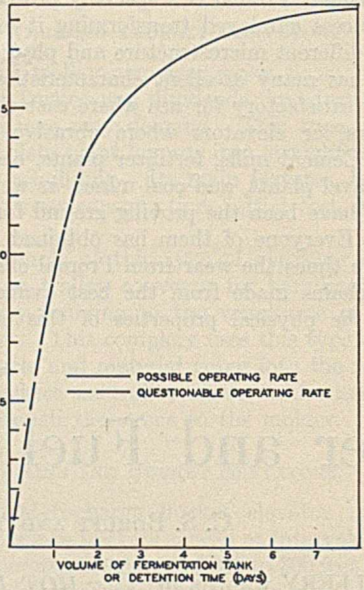


FIGURE 1. PRODUCTION OF FUEL GAS FROM BEER-SLOP WASTE. Based on continuous feeding experiments.

TABLE III. COMPARATIVE RATES OF THERMOPHILIC DIGESTION OF FRESH SEWAGE SOLIDS AND BEER-SLOP WASTE

MATERIAL	RATE OF FEEDING (Volatile Matter per 1000 cu. ft. Tank Volume per Day)	VOLUMES OF GAS RECOVERED PER TANK VOLUME PER DAY
	Lbs.	
Sewage solids (*5*)	77	1.2
Beer-slop waste	930 310	7.0 3.0

The gas from a tank having a volume twice that of the waste fed each day contains 55 per cent methane and hence has a B. t. u. of 550, which is about the same as that of coal gas (Table II). The gases from the fermentations carried out in larger tanks (4 to 6 times the volume of waste) contain a little higher percentage of methane (58). This difference in methane content is due to the fact that the volatile organic acids, which tend to remain high in a tank that is being fed at a high rate, are decomposed if held longer in the digestion tank. These acids give a higher ratio of CH_4 to CO_2 (*8*).

GAS PRODUCTION COSTS

On the basis of 50 cents a cubic foot, a 1000-cubic foot concrete digestion tank would cost $500. Such a tank should last from 10 to 20 years. This investment, at 12 per cent, would mean a yearly cost of $60, or 16.4 cents per day per 1000 cubic feet of tank capacity. The 12 per cent should easily take care of interest, amortization, and repairs.

On this basis a tank of twice the volume of the waste to be treated, and capable of delivering 7 times its volume of gas per day, would yield gas of 550 B. t. u. at a cost of 2.34 cents per 1000 cubic feet. In a tank having a volume 3 times that of the waste (Table II) more gas will be formed per unit of waste, but less gas per tank volume (5.2 volumes of gas per tank volume). This gas could be produced at a cost of 3.22 cents per 1000 cubic feet. If the industry wanted to stabilize the waste and reduce the putrefactiveness to such an extent that the sludge could be drawn into a lagoon or fill and the liquor run into the sewer or river, it would be compelled to build a tank 6 times the volume of the waste. Then 3 volumes of gas per tank volume would be produced at a cost of only 5.48 cents per 1000 cubic feet.

Table IV. Comparative Costs of Coal, Natural Gas, and Digestor Gas from Beer-Slop Waste

Fuel	Cost per 1,000,000 B. t. u.
	Cents
Soft coal (12,000 B. t. u.) at $1.50 per ton	6.2
Natural gas (1000 B. t. u.) at 15 cents per 1000 cu. ft.	15.0
Digestor gas:	
From tank, twice volume of waste	4.2
From tank, 6 times volume of waste	9.4

On a heat value basis the smaller tank would partially stabilize the waste and produce gas at a cost of 4.2 cents per 1,000,000 B. t. u. The larger tank would stabilize the waste and still deliver the fuel gas at a cost of only 9.4 cents per 1,000,000 B. t. u. These costs compare favorably with those of heat from soft coal, as well as with those of heat from natural gas piped from the southwestern states to Peoria, Ill. The cost of 1,000,000 B. t. u. of heat from soft coal having 12,000 B. t. u., at $1.50 per ton is 6.2 cents (Table IV). A gaseous fuel always has a decided advantage over a solid fuel.

The B. t. u. of gas from the fermentor could be readily increased by washing the gas with water (with or without alkali) under pressure, which would remove much or all of the carbon dioxide. This carbon dioxide could be recovered for synthetic purposes or for the production of dry ice. The residual gas (methane) could be burned or used in synthetic reactions.

Table V. Effect of Various Digestion Times (Tank Capacity) on Stability of Waste[a]

	Original Beer-Slop Waste	From Tank, Twice Vol. of Waste (2-Day Capacity)		From Tank, 4 Times Vol. of Waste (4-Day Capacity)		From Tank, 6 Times Vol. of Waste (6-Day Capacity)	
Percentage of organic matter gasified		58		67		72	
		Sludge	Liquor	Sludge	Liquor	Sludge	Liquor
pH	5.0	8.0	7.5	7.9	7.8	8.2	8.0
Total solids, p. p. m.	33,000	45,000	5,000	40,000	4,000	35,000	4000
Total volatile solids, p. p. m.	30,000	39,000	4,200	33,000	3,600	28,000	3200
Settleable solids, p. p. m.	....	....	650	....	255	....	200
Volatile acids (as acetic), p. p. m.	2,000	2,000	2,000	1,000	1,600	300	500
Ammonia nitrogen, p. p. m.	50	650	650	650	600	750	600
Total nitrogen, p. p. m.	1,600	3,000	1,000	3,000	1,000	3,000	850
Oxygen consumed, p. p. m.	16,000	10,000	3,000	....	1,300	....	1000
Immediate (30-min.) O_2 demand, p. p. m.	....	....	120	....	150	....	230
B. O. D., 5-day, p. p. m.	17,000	7,900	5,700	4,600	3,700	3,200	3000
B. O. D., 1-day, p. p. m.	6,000	2,400	1,800	1,500	1,500	1,000	1000
1-day B. O. D., mg. of O_2 per % volatile matter	2,000	615	....	454	....	357	...
Cc. gas per gram, volatile matter in 24 hours	....	44	....	28	....	....	...
Cc. gas per gram, volatile matter in 10 days	....	148	....	83	....	....	...
Moisture in sludge after draining 8 hours, %	....	70	....	80	....	84	...
Moisture in sludge after drying 3 days, %	....	51	....	....	....	66	...
Odor as drawn	....	Bad	....	Moderate	....	Slight	...
Odor after 3 days	....	Moderate	....	Slight	....	Humus	...
Volumes of sludge drawn per 100 volumes of waste fed	....	23	....	22	....	21	...

[a] Average representative analysis.

Waste Stabilization

Table V gives representative sanitary chemical data collected during a 7-month small-scale continuous feeding experiment on the gasification and stabilization of Commercial Solvent beer-slop waste.

The sludge and overflow liquor from a tank having a volume twice that of the waste fed per day (2-day capacity) was still somewhat unstable, although 58 per cent of the organic matter had been gasified. The sludge drawn from the tank was very fibrous and contained only 70 per cent moisture after having drained 8 hours on sand. After a 3-day drying (indoors) it had a moisture content of 51 per cent. The dried sludge possessed only a slight odor. The sludge had a 1-day biochemical oxygen demand (B. O. D.) of only 615 mg. per 1 per cent of volatile matter. Rudolfs and Fischer (*11*) state that a sludge of a 1-day B. O. D. of 1000 to 1500 mg. per 1 per cent of volatile matter is ready to be drawn and will not create a nuisance. The sludge as drawn produced only 44 cc. of gas per gram of volatile matter in 24 hours at 52° C. This is a lower volume than that noted for most well-digested mesophilic sewage sludges (*10*).

The overflow liquor from this tank (2-day capacity) was too unstable to be drawn into the open air. It had an average B. O. D. of 5700 p. p. m. and contained 2000 p. p. m. of volatile organic acids.

Sludge drawn from a tank having a volume 6 times that of the daily volume of waste (6-day capacity) was very stable. It was not as fibrous as that from the smaller tank (2-day capacity). After an 8-hour draining on sand it had a moisture content of 84 per cent, but after a 3-day drying (indoors) this was reduced to 66 per cent. Its 1-day B. O. D. per 1 per cent of volatile matter was 357 mg. As drawn it had only a slight sewage sludge odor, and after drying this had entirely disappeared. The liquors from this tank still had a high 5-day B. O. D. (3000 p. p. m.). Its organic content (volatile matter) was 3200 p. p. m., but the volatile organic acids were only 200 p. p. m. This overflow liquor contained but 10 per cent of the original organic matter of the waste, and was so stable that it could be run into the sewer without jeopardizing the operation of the treatment works. This additional load would still keep the organic content of the combined waste within that of normal sewage.

In addition to the routine here reported, the fairly stable fibrous sludge could be drawn from a 2-day capacity tank and only the overflow liquor from this small tank given further treatment. This method would require a much smaller total tank volume for the complete treatment of the waste, as the sludge drawn would amount to 23 per cent of the volume of the original waste fed. The volume of the tank for the final 4-day detention of the 6-day period could be proportionately decreased.

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Development of Dakota Lignite

VI. Effects of Blending and Mechanical Pressure on Coking of Lignite

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PRECARBONIZATION of Dakota lignite at 450° C. eliminates most of the carbon dioxide.

Carbonization of the char from precarbonized lignite mixed with Skelly petroleum pitch and certain bituminous coals yields a firm coke.

Mechanical pressure during carbonization has a marked effect on the structure of the solid residue.

Addition of aluminum chloride hydrate greatly aids the formation of a coke residue.

ONE of the characteristic properties of Dakota lignite is that destructive distillation produces a residue consisting of a powdery char instead of the adherent coke obtained under similar conditions from most higher rank coals. If a commercially successful process of manufacturing a suitable domestic coke from lignite could be devised, the development of the vast deposits of North Dakota would be stimulated by additional market outlets. The University of North Dakota, as part of its work in developing the mineral resources of the state, has been engaged in a study of the carbonization of lignite under different conditions for a number of years. This paper briefly presents some of the data obtained during the past three years.

Gauger and Salley (*2*) demonstrated that addition of certain inorganic materials—notably $AlCl_3 \cdot 6H_2O$—to the lignite before carbonization influenced the process so markedly that an adherent solid residue, which they termed pseudo-coke, was obtained instead of the usual powdery char. The work has since been extended to a study of the effect of blending lignite, both raw and partially carbonized, with certain organic materials for the purpose of producing a domestic coke and a suitable combustible gas.

Ordinarily the distillation of lignite yields a gas rich in carbon dioxide. It was observed in some other experimental work that carbon dioxide is given off from lignite at comparatively low temperatures, from which the senior author surmised that it might be possible to remove a large portion of this noncombustible gas by precarbonization at some temperature below that of ordinary low-temperature carbonization. A study was made of the effect of temperature on the yield and composition of gas from the destructive distillation of lignite. These experiments were carried out in an apparatus consisting of an aluminum retort, tar condenser, and gas holder with continuous-sampling device. The set-up was essentially the same as that described by Gauger and Salley (*2*).

The results which were obtained are represented graphically in Figure 1. Inspection of this figure indicates that at approximately 450° C. the ratio of carbon dioxide to total combustible gases is at a maximum. That temperature was, therefore, selected as the desirable precarbonization temperature. No attempt was made to distil at temperatures in excess of 550° C., previous experiments in the School of Mines having demonstrated that the gases contained a lower percentage of carbon dioxide at the more elevated temperatures. Thus, at 815° C. the gas distilled from Dakota lignite contained 30 per cent carbon dioxide, as against 43 per cent at 550° C. and 62 per cent at 400° C. (*1*). It must be remembered, however, that the absolute yield of carbon dioxide was higher at the higher temperatures, the variation in percentage being due to the much more rapid increase in quantity of combustible constituents with temperature.

Effects of Blending

The lignite was crushed to 0.5-cm. size and precarbonized for 1 hour at 450° C. in an iron retort. The residue was ground to pass a 14-mesh sieve and kept in sealed Mason jars until required. Table I gives the proximate analysis of the original lignite and the char (450° C.), calculated to the dry basis. Mixtures were made of this char and different tars and pitches, the method of mixing being varied to suit the material. In every case an attempt was made to insure thorough mixing.

Table I. Proximate Analyses of Lignite and Char on Dry Basis

	Volatile Matter	Fixed Carbon	Ash	B. t. u. per lb.
Original lignite	45.3	47.9	6.8	11,040
450° char	19.0	67.7	12.4	12,110

The mixture was then formed into briquets in a cupel machine and carbonized in an aluminum or nichrome retort, depending upon the temperature of carbonization. After retorting, the residue was examined and the gas analyzed. No attempt was made to obtain tar yields because of the difficulty in separating the tar from the water with any degree of accuracy.

The following materials were tested for effect upon coking of lignite char:

1. Bituminous coal-tar pitch.
2. Skelly pitch, consisting of a petroleum residue described by Rittman as "Bituminous Coal from Petroleum." The proximate analysis was volatile matter 45 per cent, fixed carbon 51 per cent, ash 4 per cent (*5*).
3. Illinois bituminous coal, received from S. W. Parr of the University of Illinois. This coal swells and blisters badly on carbonization.
4. Red Diamond coal mined in Tennessee.
5. Blue Diamond coal mined in Kentucky.
6. Gold Edge coal mined in eastern Kentucky.
7. Wheelwright coal, a gas coal mined in West Virginia and used by the local gas company.

8. Pocahontas coal from West Virginia.
9. Various pitches obtained from wheat straw.

Bituminous Coal-Tar Pitch. The results with bituminous coal-tar pitch were not very satisfactory; hence it was discarded after the early experiments.

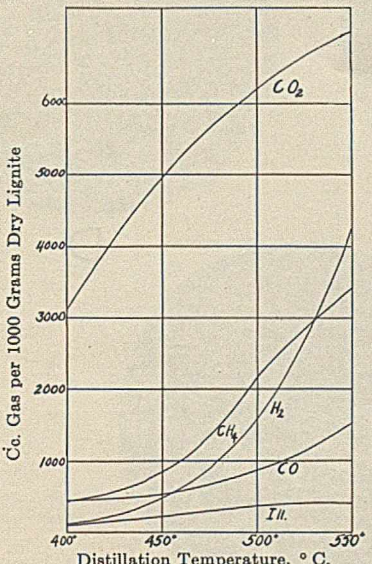

Figure 1. Effect of Temperature on Gaseous Compositions

Skelly Pitch. The results with Skelly pitch indicated a wetting of the surface of the lignite char particles by the pitch during the carbonization; hence experiments were carried out to determine the most favorable mixture and the effect of aluminum chloride on the coke structure. The best results were obtained when 25 grams of lignite char were mixed with 1.25 grams $AlCl_3 \cdot 6H_2O$ and 3 grams of pitch. Amounts below that quantity of pitch gave inferior cementing of the particles, and amounts above seemed to have no added effect on the hardness of the resulting coke.

Comparison of the results with earlier results obtained in this laboratory indicates that the proportion of $AlCl_3 \cdot 6H_2O$ required to produce a firm cokelike structure can be cut down materially (from about 20 per cent to about 4 per cent) by the admixture of 10 per cent Skelly pitch. Figure 2 shows the chars resulting from the following mixtures:

A. Lignite char alone.
B. Lignite char, 25 grams; Skelly pitch, 3 grams.
C. Lignite char, 25 grams; Skelly pitch, 3 grams; $AlCl_3 \cdot 6H_2O$, 1.25 grams.

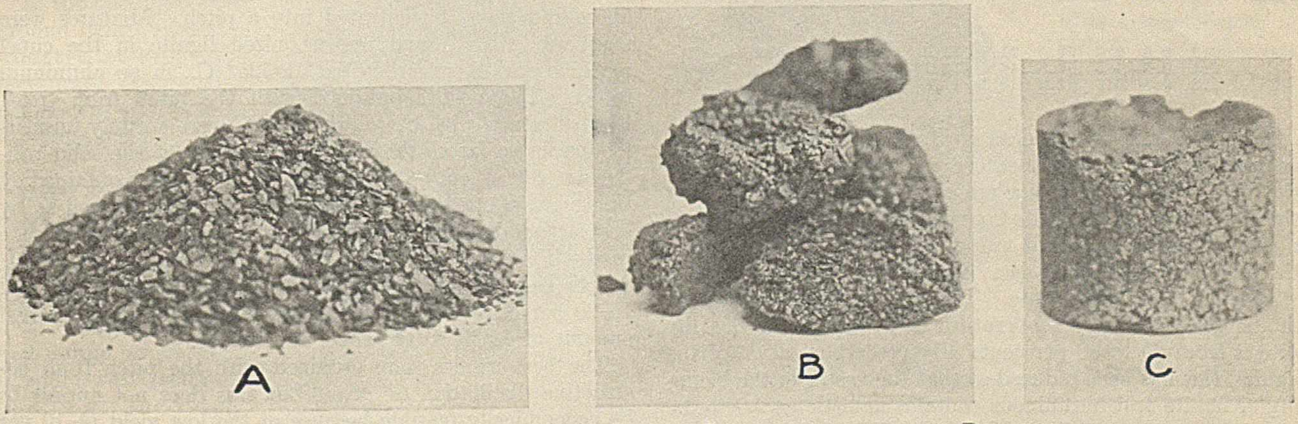

Figure 2. Residue from Coking Lignite Char, with and without Binder

Bituminous Coals. In order to obtain comparable results, the six mixtures were made up in the same proportions. Fifteen grams of lignite char, 10 grams of the bituminous coal, and 8 grams of water composed the mix of the first series.

Illinois bituminous gave a friable soft coke with very little cementation of the lignite and the bituminous. Red Diamond, Blue Diamond, and Gold Edge gave practically the same structure. All were hard, lustrous, of relatively dense structure, and gave the characteristic metallic ring. However, the porous structure of true coke was not very pronounced. Wheelwright coal showed considerable evidence of coking, which was accompanied by a slight swelling. The blend with Pocahontas gave a true coke structure. The resulting coke showed considerable swelling, and the porous structure was very pronounced. A microscopic examination seemed to indicate that the blending was complete and that the coal and char are completely miscible.

In order to determine the effect of aluminum chloride hydrate on the carbonization and subsequent coking of the different blends, a second series was made with the following mix: 15 grams lignite char, 10 grams of the coal to be blended, 1.25 grams of $AlCl_3 \cdot 6H_2O$, and 8 grams of water.

The cokes resulting from the blend plus aluminum chloride hydrate are all of a harder denser structure than the blends alone. This is particularly noticeable in the case of the Pocahontas-lignite blend where the difference is very pronounced.

The apparent complete blending of the Pocahontas and lignite gave a coke structure that was worthy of further study. A series was run, varying the amount of Pocahontas in the blend in order to determine how little Pocahontas could be added and still have the characteristic coking. The mixes used were:

Mix	Lignite Char *Grams*	Pocahontas *Grams*	Water *Grams*
A	15	10	8
B	16	9	8
C	17	8	8
D	18	7	8
E	19	6	8
F	20	5	8

Figure 3 shows photomicrographs of five of the resulting chars. The letters below the photographs correspond to the letters in the above table showing the mixes. All were magnified approximately 15 diameters. The first three mixtures showed considerable evidence of swelling and gave a good hard-coke structure. D, E, and F showed no evidence of swelling and, though blending was evidenced, there was apparently not enough binder to make the characteristic

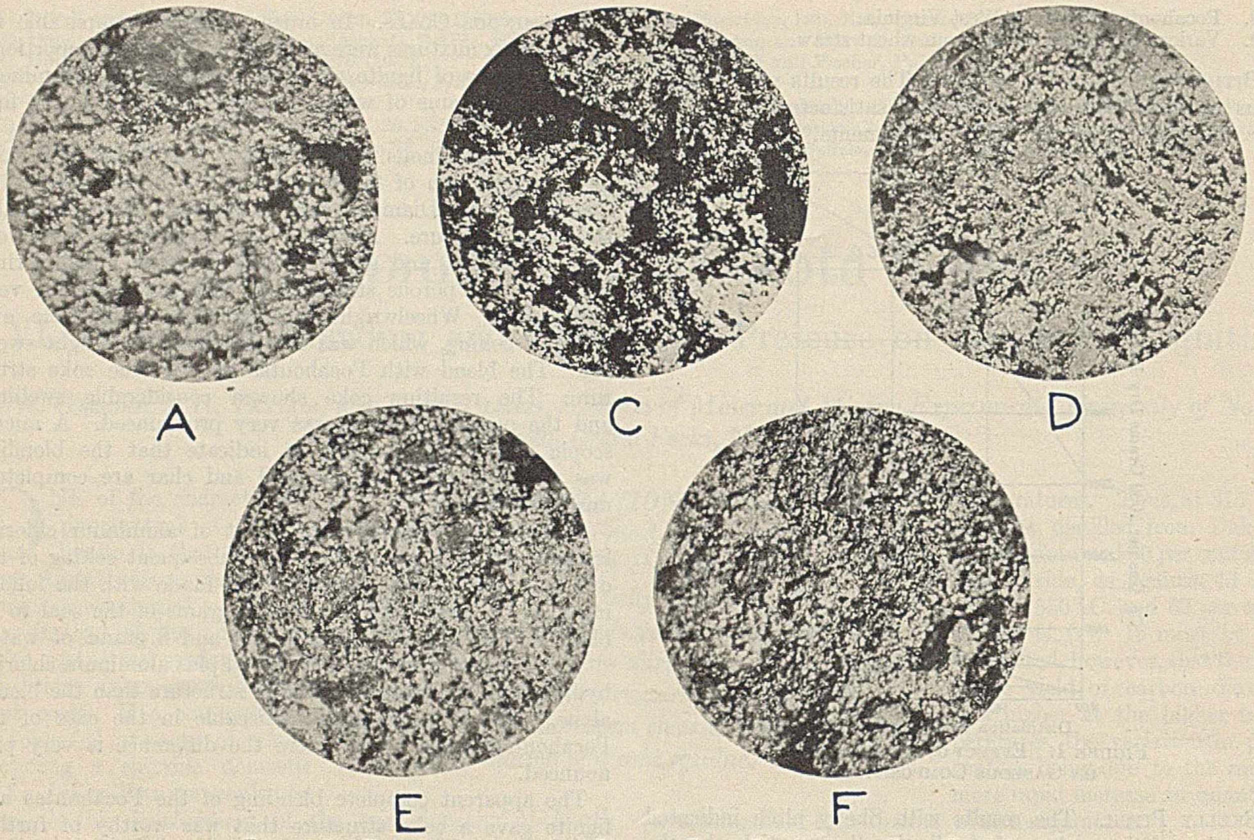

FIGURE 3. PHOTOMICROGRAPHS OF LIGNITE CHAR–POCAHONTAS COAL COKES

hard porous coke structure. Mix C, which has the ratio of non-coking to coking of 68:32, compares very favorably with the 70:30 ratio as found by Lander and McKay (*3*).

Table II gives the analysis of the gas from the carbonization of three of the above blends.

TABLE II. GAS DATA

							VOLUME OF GAS:		CALCULATED THERMAL VALUE
BLEND	CO_2	ILL.	O_2	H_2	CO	CH_4	Per 100 grams blended coal	Per ton blended coal	
							Cc.	*Cu. ft.*	*B.t.u./cu. ft.*
A	2.3	0.5	2.0	72.5	11.9	11.2	33,300	10,699	409
E	2.1	0.8	1.5	67.8	14.0	13.1	33,200	10,624	409
F	2.8	0.3	0.5	62.2	13.3	11.8	32,800	10,196	370

Although the volume data in Table II cannot be taken as quantitatively exact because of leakage in the retort, the results are in close enough agreement to indicate that the carbonization of lignite char with Pocahontas coal gives a gas of high enough heat value to be easily carbureted to the standards set for city gas. The carbon dioxide content is worthy of particular note. The carbon dioxide content of the gas from high-temperature carbonization of raw lignite is from 20 to 30 per cent. By precarbonization of the lignite, this has been reduced so that the gas from the blending of lignite and bituminous contains as little as 2.0 to 3.0 per cent carbon dioxide. This reduction greatly increases the heat value and reduces the inert content of the gas.

The proximate analysis of the coke resulting from Blend A is as follows:

VOLATILE MATTER	FIXED CARBON	ASH	B. T. U. PER LB.
3.16	86.01	10.82	13,060

WHEAT-STRAW PITCHES. Wheat straw constitutes one of the abundant waste materials produced in North Dakota. Since it is composed largely of cellulose fibers, resins, and lignin, the manufacture of a binder for coking lignite from it seemed entirely feasible. In order to disintegrate the straw, the following treatments were used:

Heating with caustic soda solution under pressure.
Heating with sodium sulfite solution under pressure.
Heating with steam under pressure.
Destructive distillation.

The tar liquors were separated from the disintegrated fibers and then concentrated into a pitch. Mixtures were made up with ground precarbonized lignite in the cupel machine and then carbonized at 525° C., in an aluminum retort. The results obtained with the pitch from treatment of straw with chemical reagents were entirely unsatisfactory in so far as the physical structure of the solid residue was concerned. On the other hand, the pitch obtained by treatment of straw with steam under pressure, as well as by destructive distillation, proved to be very effective in coke production. The most favorable mixture proved to be 80–84 per cent precarbonized lignite, ground to 30 mesh, and 16–20 per cent straw pitch, either with or without a small amount of $AlCl_3 \cdot 6H_2O$ added as catalyst.

The best results were obtained with the pitch from destructive distillation of straw, but this does not appear to be economically feasible because of the low yield (4–10 per cent) of the weight of straw. Since the steam digestion produces a disintegrated cellulose fiber that can be used in the manufacture of insulating and pulp board, such an industry would furnish a by-product which could be used in coking lignite.

EFFECT OF MECHANICAL PRESSURE ON CARBONIZATION

Experiments indicated that the pressure of briquetting had a favorable influence on the coke structure. Because of this fact, studies were made of the effect of mechanical pressure during the carbonization process on the structure of the residue.

The apparatus used consisted of an iron pipe, 12 inches (30.48 cm.) long and 1 inch (2.54 cm.) inside diameter, with iron plungers in each end. The prepared lignite was placed between the plungers which were compressed in a Riehle testing machine. The iron pipe was placed within an electric furnace whose temperature could be controlled by means of a rheostat. A thermocouple was placed on the outside of the iron pipe and consequently registered temperatures slightly above that of the lignite.

The lignite used in the pressure-heat treatment was previously dried on a hot plate and ground to various sizes. The prepared lignite, amounting to about 30 grams in each test, was placed between the two plungers, and the sample then given a preliminary compression at a pressure usually greater than that used while heating. After the preliminary compression, the coal was heated slowly and a proper pressure maintained by means of the adjusting wheel. Heating was continued until reaction, as evidenced by evolution of volatiles, almost ceased. This required about 75 minutes and occurred at a temperature of about 540° C. The pipe and plungers were then removed and cooled. The coal product was forced out of the pipe. The briquetting pressure was recorded, as well as the coking pressure and temperature.

On heating, the coal did not show indication of much evolution of gas until about 100° C. was reached, when moisture and gases were expelled. This caused a release of the resistance of the coal to the pressure, and the faces of the machine were then brought close enough together to maintain the desired pressure. The evolution diminished until about 380° C. was reached, when there was a sharp increase of softening and expulsion of gases. This continued until about 450° C., when reactions began to cease, and there was not much loss of pressure owing to contraction of the coal mass. About 1 hour and 45 minutes were required to reach a temperature of 500° C.

During the course of these experiments, the effects of the following variables on the final solid residue were studied: preliminary pressure, pressure and temperature of carbonization, particle size, blending with tars and coking coals, and previous treatment of the lignite. In general, the tests were successful, not only in producing a coherent solid residue but also in giving some information as to the nature of lignite and its relationship to other coals. The results demonstrated that Dakota lignite contains compounds from which (under conditions that are possible in nature) high-rank coals may form.

In the first tests, the ground lignite was briquetted at an initial pressure of 5000 pounds per square inch (351.5 kg. per sq. cm.). The briquet was then carbonized under varying conditions in an attempt to obtain a satisfactory product. The results of the experiments indicated that a high initial briquetting pressure was essential, and in all the later tests a preliminary pressure of 20,000 pounds per square inch (1406 kg. per sq. cm.) was used.

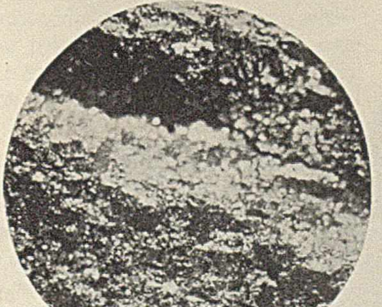

FIGURE 4. PHOTOMICROGRAPH OF LIGNITE CARBONIZED UNDER MECHANICAL PRESSURE

The carbonization conditions were varied to determine the values necessary to give a suitable product. It was found that a balance could be reached between the temperature and pressure necessary to obtain a good product; the coking pressure could be reduced to some extent by increasing the temperature, and vice versa. By using a maximum temperature of 600° C., a suitable coke was formed with a pressure of 636 pounds per square inch (44.7 kg. per sq. cm.). However, pressures below this did not produce hard coke even though higher temperatures were used. With a temperature of 670° C., and pressure of 382 pounds per square inch (26.9 kg. per sq. cm.), a soft product was obtained. These results indicate the importance of pressure in the coking of lignite and point toward a method of using the coking constituents which are not effective otherwise. The best coke obtained had been carbonized under a pressure of 1920 pounds per square inch (135 kg. per sq. cm.) and a temperature of 600° C. The homogeneous bitumen-like appearance of the fractured surface is illustrated in Figure 4, which is a photograph of a magnified view of the sample. Temperatures of 530° and 550° C. gave excellent products which were very hard and had the appearance of a semi-bituminous coal.

The size of the lignite particles had much influence on the nature of the product. The smaller-size particles gave the best structure. With a lignite ground to 10 mesh and a pressure ranging from 636 to 1920 pounds per square inch (44.7 to 135 kg. per sq. cm.), no satisfactory coke was obtained, although with 20-mesh lignite very good products resulted under similar conditions. This may be explained by the fact that the coarse grains do not pack as tightly as finer particles, and the tar vapors have more chance to escape.

In the majority of tests the lignite used had been dried over a hot plate, thereby losing the largest portion of the moisture. A small amount of moisture was purposely left in the coal, as it might aid the coking reactions and packing of lignite particles. In some experiments steam-dried lignite prepared by the Fleissner method (*4*) was ground and used. The product obtained was unsatisfactory and crumbled in removal from the apparatus. In all instances the cokes were inferior to those of air-dried lignite in which the same conditions, such as particle size, temperature, and pressure, were maintained. These tests indicate the destruction of some of the coking constituents in the steam-drying process.

The blending of various materials was studied in a series of tests. Tars and coking coals were added for the purpose of determining their relative effects. In two tests lignite tar was added to lignite in the amount of about 3.2 per cent. With a temperature of 382° C. a soft coke was formed, while a temperature of 636° C. gave a good coke. The products, however, were not perceptibly better than those of lignite alone, treated under the same conditions.

Tests were made to determine the nature of the cementation in the pressure carbonization. There was a possibility that the lignite tar permeated the pores within the mass and was not altered appreciably. This was not true, however, for, upon grinding and recoking a sample, it did not form a coherent coke, indicating that the coking constituents were broken down in the previous treatment.

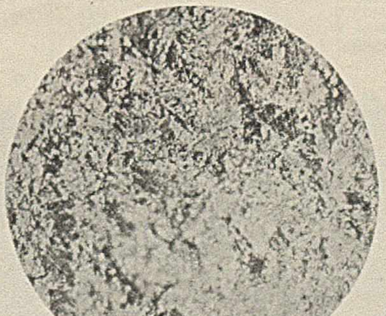

FIGURE 5. LIGNITE CHAR–POCAHONTAS COAL BLEND CARBONIZED UNDER PRESSURE

A mixture of char with 6.25 per cent of Pocahontas coal produced a very good coke under ordinary conditions of pressure carbonization. Figure 5 shows the glossy well-cemented surface resembling that of a high-rank coal. This small amount of the coking blend was sufficient in this method, whereas a value of about 20 per cent would be necessary to produce the same grade of coke with heat treatment alone.

TABLE III. PRESSURE CARBONIZATION OF LIGNITE

SAMPLE	CONSTITUENTS				COKING			
	Lignite		Pocahontas		Lignite pitch	Pressure	Temperature	Results[a]
	Grams	*Mesh*	*Grams*	*Mesh*		*Lbs.*	*° C.*	
20	100	10	..	..	..	1920	450	Soft coke
21	100	10	..	..	..	636	450	Friable
22	100	20	..	..	..	1920	530	Very good
23	100	20	..	..	..	382	450	Soft
24	100	20	..	..	..	1272	550	Fair
25	100	..	..	..	..	1920	550	Quite good
27	30	..	..	..	1	636	600	Good
28	30	..	..	..	1	382	670	Soft
29	30	..	3	..	..	382	670	Quite firm
30	(Lignite char)	..	..	..	..	1272	500	No good
31	40	20	..	..	..	0–636[c]	500	Poor
32	70	14	30	28	..	1920	500	Good coke
33	35	20	..	..	..	1920	600	Good
36	100	14	..	..	..	0–1272[c]	500	Fair
37	Portion of lignite precoked by same method				..	1920	900	Undesirable
38	28[b]	14	12	28	..	1920	550	Very good
39	50[b]	14	10	28	..	636	500	Poor
45	30	14	3	28	..	636	550	Very good
46	30	14	3	28	..	636	650	Very good
47	Steam-dried lignite				..	1272	500	Broken-top hard
48	30	14	2	28	..	636	800	Fair

[a] Sample 20 was subjected to a preliminary pressure of 5090 pounds per square inch (358.9 kg. per sq. cm.) before carbonizing; all the others to preliminary pressure of 20,000 pounds per square inch (1406 kg. per sq. cm.).

[b] Char.

[c] Intermittent.

A variable pressure was used in several experiments to determine the effect upon the coke formed. It was thought that, by varying the pressure during the coking, a better coke would result. In one test the pressure was applied between 0 and 500 pounds per square inch (35.2 kg. per sq. cm.) during the heating period with a briquetting pressure of 15,000 pounds per square inch (1054.5 kg. per sq. cm.). The result was an inferior product which easily crumbled. Another test was made with a pressure ranging from 0 to 1000 pounds per square inch (70.3 kg. per sq. cm.) in cycles of about 2 minutes. A fair coke was formed, but it was inferior to others formed under the same conditions, except for variation in pressure—namely, 15,000 pounds per square inch (1054.5 kg. per sq. cm.) preliminary pressure, a temperature of 500° C., but with constant coking pressure of 1000 pounds per square inch (70.3 kg. per sq. cm.)

The results of the pressure-carbonization tests on lignite, including variation of conditions, additions of binding materials, and their effects are given in Table III. The proximate analysis of a sample of coke made under favorable conditions from lignite alone was as follows:

Moisture, %	4.9
Ash, %	10.4
Volatile matter, %	18.4
Fixed carbon, %	66.3
Thermal value, B. t. u. per lb.	11,676

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RECEIVED August 28, 1931. Presented before the Division of Gas and Fuel Chemistry at the 82nd Meeting of the American Chemical Society, Buffalo, N. Y., August 31 to September 4, 1931. A. W. Gauger's present address is School of Mineral Industries, Pennsylvania State College. This paper is from the theses of J. R. Taylor and C. W. Ulmen, submitted in partial fulfilment of the requirements for the degree of master of science in chemical engineering.

A FIELD OF DAHLIAS AT CUDAHY, CALIF.

Dahlias are not now considered as a source for commercial levulose, but the plant resembles somewhat the Jerusalem artichoke. The dahlia is a satisfactory source of inulin, a unique sugar which finds a place in diagnosis and which assumed great importance during the World War.

Commercial Production of Levulose

II. Conversion of Jerusalem Artichoke Juices

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Department of Chemistry, Iowa State College, Ames, Ia.

THE FACTORS controlling the conversion reaction of Jerusalem artichoke juices have been determined. The decomposition of levulose under conditions of high acidity and temperature has been studied, and the limiting conditions have been ascertained. Results of conversion experiments run under varying conditions of concentration and acidity are here presented.

Normality-pH data for different concentrations of juice treated with varying quantities of sulfuric and hydrochloric acids have been determined. The amount of sulfuric or hydrochloric acid required to convert a juice of any concentration from 4 to 40 per cent total solids in 1 hour at 80° C. has been calculated. Enough data for similar calculations for other periods of time are presented.

WHEN the study of the preparation of levulose (*2*) from the Jerusalem artichoke (*Helianthus tuberosus*) was undertaken at Iowa State College very little information on the conversion of the inulin and other levulose-yielding carbohydrates to levulose was available. Work on the hydrolysis of pure inulin had been reported, but this was of no value as the process adopted required the direct conversion of all the polysaccharides, rather than the preliminary isolation of the inulin.

A limited investigation of this problem had been reported by Jackson, Silsbee, and Proffitt (*1*), who concluded that the resultant of the reactions occurring during the conversion process follows substantially the course of a unimolecular reaction. They reported a number of velocity constants for various conditions of acidity and temperature. (Concentration of juice was not given.) These workers observed that the velocities vary widely with the composition and concentration of the juice. For this reason their published constants are of little practical value.

DETERMINATION OF VELOCITY CONSTANTS

In accordance with the usual procedure, a quantity of juice was heated and kept at the desired temperature. The required quantity of acid was added and portions were withdrawn from time to time for polarization. Clarification was accomplished by means of a solution of normal lead acetate, as recommended by Jackson, Silsbee, and Proffitt (*1*), using the following method:

> Support flasks of 500 cc. capacity in a constant-temperature bath and equip them with stirrers. Place 360 cc. of juice in a flask and allow it to heat up to the temperature of the bath (80° C.). Add 40 cc. of 0.9495 *N* hydrochloric acid. At the end of 5 minutes remove 10 cc. of the mixture with a pipet and add to 10 cc. of 0.2 saturated *N* lead acetate solution. Cool the sample rapidly to room temperature and filter through a small filter paper.

This procedure gave a very satisfactory clarification and the solution was readily polarized in a 100-mm. tube. At appropriate intervals other samples were withdrawn, clarified, filtered, and polarized.

Jackson showed that velocity constants for the rate of conversion of Jerusalem artichoke juices may be computed by means of the familiar equation for monomolecular reactions:

$$K = \frac{1}{0.4343\,t} \log \frac{R_0 - R_\infty}{R_t - R_\infty}$$

Table I gives the data obtained and the constants computed for two runs. The constants, 0.0137 and 0.0135, are typical of the checks obtained in other duplicate runs and indicate the precision to be expected in data of this type. Although the individual constants may vary as much as four units in the second significant figure, the averages agree very closely.

TITRATABLE ACIDITIES OF RAW AND CONVERTED JUICES

In the work of Jackson and his associates the amount of acid used was designated as the "apparent" acidity, or the acidity which would have been produced in pure water. In their words, "a portion of the acid in each instance was rendered ineffective by inorganic impurities." Several titrations were made to test the soundness of this assumption, the results of which are given in Table II.

TABLE I. VELOCITY CONSTANTS FOR RATE OF CONVERSION OF ARTICHOKE JUICE (14.4 PER CENT TOTAL SOLIDS) WITH 0.095 *N* HCl AT 80° C.

RUN	TIME	ROTATION OBSERVED	$R_t - R_\infty$	$\log\frac{R_0 - R_\infty}{R_t - R_\infty}$	$K = \frac{1}{0.4343\,t}\log\frac{R_0 - R_\infty}{R_t - R_\infty}$
	Min.				
1	0	+2.2	10.0	.....	....
	5	+1.5	9.3	0.03152	0.0145
	20	−0.4	7.4	0.13077	0.0150
	45	−2.5	5.3	0.27572	0.0142
	85	−4.9	2.9	0.53760	0.0146
	120	−5.8	2.0	0.69897	0.0135
	190	−6.7	1.1	0.95861	0.0117
	315	−7.6	0.2	1.69897	0.0125
	∞	−7.8	..	.....	....
Average	..	...	..	.....	0.0137
2	0	+2.0	9.7	.....	....
	20	−0.4	7.3	0.12345	0.0143
	50	−2.9	4.8	0.30553	0.0141
	85	−4.4	3.3	0.46826	0.0127
	115	−5.6	2.1	0.66455	0.0134
	185	−6.8	0.9	1.03253	0.0129
	285	−7.5	0.2	1.68574	0.0136
	∞	−7.7	..	.....	....
Average	..	...	..	.....	0.0135

TABLE II. NORMALITIES DETERMINED BY TITRATING WITH STANDARD NaOH SOLUTION

TOTAL SOLIDS	ACIDITY				
	Raw juice	Acid added	Total	By actual titration	By difference
%					
7.2	0.0143	0.0950	0.1093	0.1020	0.0073
14.4	0.0238	0.0950	0.1188	0.1088	0.0100
18.0	0.0306	0.0950	0.1256	0.1212	0.0044
26.1	0.0445	0.0950	0.1395	0.1292	0.0103

The data in Table II show that the actual titratable acidity of a converted juice is practically equal to the initial acidity of the raw juice plus that of the acid added. If it is true that a more concentrated juice has a lower velocity constant than a less concentrated juice at the same acidity, it is necessary to look to factors other than the titratable acidity for the explanation.

CONVERSION WITH HYDROCHLORIC ACID

Velocity constants were obtained for the rates of conversion of artichoke juices with hydrochloric acid at 80° C. (Table III). Two series of determinations were made. In the first the acidity was held constant while the concentration of the juice was varied. In the second the acidity was varied and the concentration held constant. The pH values of the converted juices were obtained by means of the quinhydrone electrode in the usual manner.

TABLE III. CONVERSION OF ARTICHOKE JUICES WITH HCl AT 80° C.

TOTAL SOLIDS IN JUICE (REFRACTOMETER)	APPARENT NORMALITY	VELOCITY CONSTANT	pH (QUINHYDRONE ELECTRODE AT 25° C.)
%			
7.2	0.095	0.1680	1.68
14.4	0.095	0.0136	2.80
18.0	0.095	0.0053	3.19
26.1	0.095	0.0015	3.83
14.4	0.0475	0.0009	4.10
14.4	0.0950	0.0136	2.80
14.4	0.1425	0.0690	2.09
14.4	0.1900	0.2310	1.55

The first four figures in column 3 show a hundred fold increase in the velocity constant for a juice of 7.2 per cent total solids, as compared with a juice of 26.1 per cent total solids, the apparent normality being constant. This vast difference shows that values of the velocity constants are worthless unless the concentration of juice is specified.

When the concentration of juice was held constant and the apparent acidity varied, it was to be expected that the velocity constant would increase with the acidity.

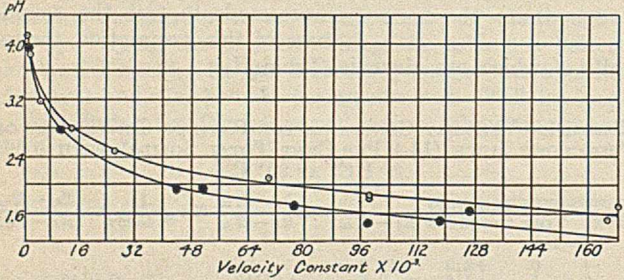

FIGURE 1. VELOCITY CONSTANT–pH CURVES (80° C.)

⊙ Hydrochloric acid ● Sulfuric acid

A study of the pH values obtained indicates definitely that the reason for the differences in the velocity constants for different concentrations of juice at the same apparent normality is to be found in the buffer action of certain constituents of the raw juice.

CONVERSION WITH SULFURIC ACID

For the conversion of artichoke juices on a large scale of operations, sulfuric acid has a number of advantages which should not be overlooked. In addition to being the cheapest of all acids, it is precipitated out as the insoluble calcium sulfate when the converted juice is neutralized with hydrated lime. Thus it does not add to the dissolved impurities as some other acids do.

Table IV gives the results of eight velocity constant determinations made with varying strengths of sulfuric acid and varying concentrations of juice.

TABLE IV. CONVERSION OF ARTICHOKE JUICES WITH H_2SO_4 AT 80° C.

TOTAL SOLIDS IN JUICE (REFRACTOMETER)	APPARENT NORMALITY	VELOCITY CONSTANT	pH (QUINHYDRONE ELECTRODE AT 25° C.)
%			
14.4	0.0573	0.0013	3.92
14.4	0.1147	0.0109	2.77
14.4	0.1720	0.0513	1.95
14.4	0.2294	0.1270	1.61
30.8	0.1560	0.0107	2.77
30.7	0.2364	0.0433	1.94
30.6	0.3150	0.0973	1.45
30.5	0.3940	0.2170	1.23

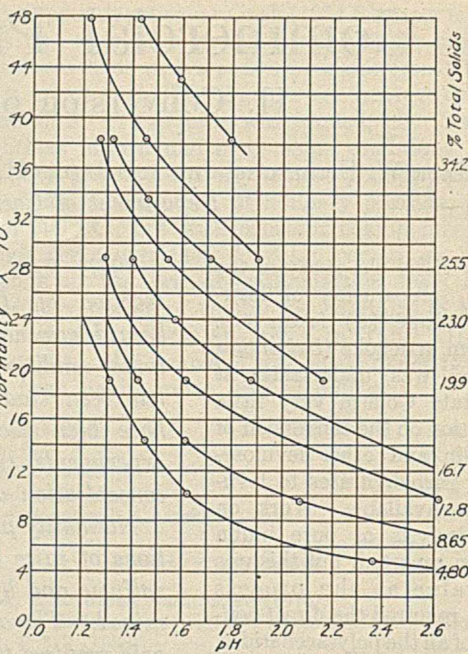

FIGURE 2. ARTICHOKE JUICES TREATED WITH SULFURIC ACID

The constants in lines 2 and 5 of Table IV are practically identical. The pH values corresponding to these constants are the same, although one juice contains 14.4 per cent total solids and 0.1147 *N* acid, while the other contains 30.8 per cent total solids and 0.1560 *N* acid. This suggests the possibility that the velocity constant depends only upon the pH of the mixture of acid and juice.

DECOMPOSITION OF LEVULOSE DURING CONVERSION

Approximately 12 grams of levulose (prepared in this laboratory) were dissolved and diluted to 200 cc., placed in one of the conversion flasks in the water bath, and brought up to 80° C. Then 10 cc. were removed and polarized. One cc. of 23.6369 *N* sulfuric acid was added to the rest of the 6 per cent levulose solution, and polarizations were made at the intervals shown in Table V. For the next run approximately 24 grams of the same levulose were dissolved and diluted to 200 cc. and 2 cc. of the 23.6369 *N* sulfuric acid were added after 10 cc. of the original solution had been removed and polarized. This run was repeated at 90° C. The results are given in Table V.

TABLE V. DECOMPOSITION OF LEVULOSE SOLUTIONS

TIME	ROTATION
Minutes	° *V.*
6 PER CENT SOLUTION AT 80° C. AND PH 1.31	
0	−11.4
15	−11.4
37	−11.4
120	−11.4
195	−11.4
12 PER CENT SOLUTION AT 80° C. AND PH 1.12	
0	−22.0
15	−22.0
45	−22.0
80	−22.0
130	−21.7
12 PER CENT SOLUTION AT 90° C. AND PH 1.12	
0	−21.0
15	−18.9
30	−18.3

The data in Table V show that at temperatures up to 80° C. and pH values down to 1.12 the amount of levulose destroyed in 60 minutes is insignificant. The conversion experiments reported so far in this work indicate that it will never be necessary to exceed these conditions in prac-

Table VI. Effect of Concentration of Juice on pH

Total Solids in Juice	H_2SO_4 Added						HCl Added					
	Sol. A		Sol. B		Sol. C		Sol. A		Sol. B		Sol. C	
%	N[a]	pH	N[a]	pH	N[a]	pH	N[a]	pH	N[a]	pH	N[a]	pH
4.8	0.1016	1.62	0.1916	1.31	0.0479	2.36	0.0768	1.60	0.1536	1.16	0.0384	2.54
8.65	0.0958	2.07	0.1916	1.42	0.1437	1.61	....	..	....	..	....	..
12.8	0.0977	2.62	0.2894	1.29	0.1916	1.61	0.1536	1.56	0.2304	1.13	0.0768	3.09
16.7	0.1916	1.87	0.2875	1.40	0.2396	1.57	....	..	....	..	....	..
19.9	0.1916	2.16	0.3833	1.27	0.2875	1.54	0.2304	1.49	0.3072	1.07	0.1536	2.48
23.0	0.2875	1.71	0.3833	1.32	0.3354	1.46	....	..	....	..	....	..
25.5	0.3833	1.45	0.2875	1.90	0.4791	1.23	0.3840	1.00	0.2304	2.08	0.3072	1.35
34.2	0.4791	1.43	0.3833	1.79	0.4312	1.59	....	..	....	..	....	..

[a] Normality.

tical work, as juices of any concentration may be completely converted at pH values above 1.12 in 60 minutes or less.

Conversion as a Function of pH

Plotting pH values (Figure 1) against the corresponding velocity constants for various concentrations of juice and acid at a temperature of 80° C., both sulfuric and hydrochloric acids being used, shows that the velocity constant is a function of pH only for each acid. The fact that the two acids form separate curves is presumedly to be attributed to the relative influences of the negative ions.

Conversion Process Control

In connection with the semicommercial production of levulose at Iowa State College, it was desired to convert batches of juice in exactly one hour, regardless of the concentration of the juice. The velocity constant required for 99.9 per cent conversion in 60 minutes may be computed as follows:

$$K = \frac{1}{0.434\ (60)} \log \frac{1000}{1} = 0.115$$

At 80° C. a constant of 0.115 is obtained at pH 1.5 when sulfuric acid is used, or at pH 1.75 when hydrochloric acid is used (Figure 1).

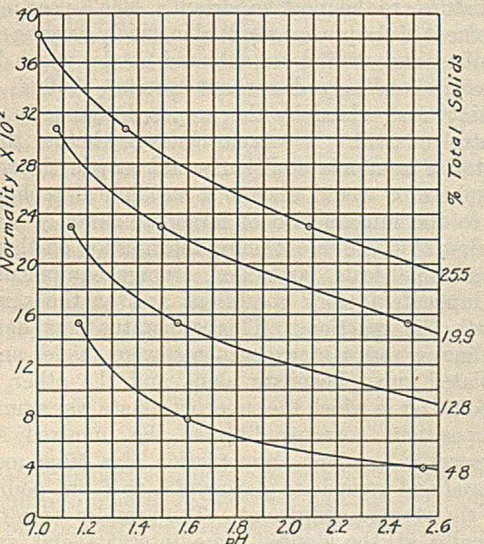

Figure 3. Artichoke Juices Treated with Hydrochloric Acid

To make it possible to produce any desired pH value in a juice of any given concentration, a number of experiments was performed. A series of juices was made up, various proportions of acid were added, and the pH values were measured by means of the quinhydrone electrode. The results are presented in Table VI and in Figures 2 and 3.

The normalities corresponding to pH values of 1.5 were obtained by interpolation from the curves of Figure 2. Plotting these normalities against the corresponding concentrations of juice gave a straight line. Accordingly, the amount of acid required to produce a definite pH is directly proportional to the concentration of the juice, as measured by the refractive index.

By interpolation and extrapolation, the amount of acid required to produce pH 1.5 for a juice of any concentration may be computed. Table VII shows the values for apparent normality thus obtained. The data for hydrochloric acid were treated in the same manner. Column 3 of Table VII gives the apparent normalities required to produce pH 1.75 by the use of hydrochloric acid. The apparent normalities are those that would have been produced in pure water.

Table VII. Apparent Normality of Acid Required for 99.9 Per Cent Conversion in 1 Hour at 80° C.

Total Solids	Apparent Normality		Total Solids	Apparent Normality	
	H_2SO_4	HCl		H_2SO_4	HCl
%			%		
4	0.120	0.058	23	0.332	0.238
5	0.131	0.067	24	0.343	0.248
6	0.142	0.077	25	0.354	0.257
7	0.153	0.086	26	0.365	0.267
8	0.164	0.096	27	0.376	0.276
9	0.175	0.105	28	0.388	0.286
10	0.187	0.115	29	0.399	0.295
11	0.198	0.124	30	0.410	0.305
12	0.209	0.134	31	0.421	0.314
13	0.220	0.143	32	0.432	0.324
14	0.231	0.153	33	0.443	0.333
15	0.242	0.162	34	0.454	0.343
16	0.254	0.172	35	0.465	0.352
17	0.265	0.181	36	0.476	0.362
18	0.276	0.191	37	0.487	0.371
19	0.287	0.200	38	0.498	0.381
20	0.298	0.210	39	0.509	0.390
21	0.309	0.219	40	0.521	0.400
22	0.321	0.229			

Composition of Juice

The juice for the experimental work reported in this paper was prepared from dried artichoke chips by means of a small diffusion battery of 6 to 8 cells. The battery was operated in the usual manner, so that fresh water came in contact with the most nearly exhausted chips, while the concentrated juice passed through the fresh chips. In some cases juice was obtained by a similar process, using beakers in a water bath. The juice was usually made up fresh for each experiment. The only necessary precaution was to see that the chips were completely exhausted before being discarded. As concordant results were obtained throughout the work, it is evident that minor differences in composition, such as would be met in the day-to-day operation of a commercial plant, are of no consequence.

A quantity of juice (19.6 per cent total solids) was prepared by soaking dried artichoke chips in hot water for 45 minutes and pressing them in a small screw press. This produced a juice of different composition because some of the soluble material remained in the pulp. According to Table VII, an apparent normality of 0.292 with sulfuric acid should produce a pH of 1.5 and a velocity constant of 0.115. The pH was found to be 1.29 and the velocity constant was 0.234. With either sulfuric or hydrochloric acid the resulting pH value was found to be practically 0.2 of a unit lower than for juice obtained in the ordinary manner.

The data presented in this paper cannot be expected to apply to any juice having a composition greatly different from those of the juices used in the work here reported.

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(1) Jackson, Silsbee, and Proffitt, *Bur. Standards Sci. Paper* **519** (1926).

(2) McGlumphy, Eichinger, Hixon, and Buchanan, IND. ENG. CHEM., 23, 1202 (1931).

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Available Phosphoric Acid Content of Ammoniated Superphosphate

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THE EFFECT of temperature and time of storage, of moisture content, and of grade of mixed fertilizers on the availability of the phosphoric acid in ammoniated materials has been determined. Comparative data were obtained by both the official method of analysis and the proposed method tentatively adopted in October, 1930, by the Association of Official Agricultural Chemists. The rate at which ammoniated products reach final equilibrium can be varied from 12 months at low temperatures to 5 days at elevated temperatures. The moisture content is also of importance in determining this rate.

NEARLY two years ago it was found that ammoniated superphosphate exhibited analytical irregularities not existent in unammoniated phosphates. The investigation of these peculiarities and subsequent vegetation tests under the direction of the United States Department of Agriculture and several state agricultural experiment stations led the Association of Official Agricultural Chemists in October, 1930, tentatively to adopt a modified method of analysis for available P_2O_5 in fertilizers. The significance of this change with respect to industrial ammoniation technic and factory data on the reversion of phosphates under the proposed method were practically unknown.

This paper contains data on: (1) Comparative analyses of ammoniated materials under both official and proposed methods; (2) influence of temperature, length of storage, moisture, and degree of ammoniation on the rate and extent of phosphate reactions in ammoniated superphosphates; (3) effect of mixture grade (ratio of ammoniated super to total weight) on the analytical determinations of insoluble P_2O_5; (4) results of factory tests to determine mechanical aspects of significance in the addition of larger amounts of ammonia; (5) correlation of previously derived theoretical equations and data with present results.

RECENT LITERATURE

The patent and journal literature up to 1930 has already been reviewed (*6*). The calcium phosphates formed by ammoniation reactions were shown by Jacob et al (*4*) to be hydroxy or basic compounds of characteristics different from those of the naturally occurring rock phosphates. Ross and Jacob (*10*) reported that preliminary pot and field tests indicated these basic phosphates to be at least 75 per cent efficient (water-soluble phosphates, 100 per cent efficient). Comparative analytical behavior, with respect to solubility in neutral ammonium citrate solution, of all types of phosphatic fertilizer materials was determined by Jacob et al (*5*). Haskins (*2*), Salter (*11*), Buie (*1*), and Parker (*9*) described experiments on the agricultural availability of the less soluble forms of calcium phosphates. Salter (*12*) also showed the citrate solubility of calcium phosphates to be strongly influenced by the presence of other soluble calcium compounds, and suggested the addition of ammonium oxalate to the citrate solution as a means of obtaining consistent results. Howes and Jacobs (*3*) indicated the effect of increasing the acidity of citrate solutions, as well as of changing the citrate phosphate ratio, on the insoluble P_2O_5 found in ammoniated materials. Technical phases of the ammoniation process, including diagrams and photographs of factory installations, have been presented (*7*, *8*).

PLAN OF INVESTIGATION

Previous work (*6*) had resulted in fairly definite conclusions as to the chemical reactions in ammoniated superphosphates. Little was learned of the controlling factors, however, beyond the general knowledge that temperature and moisture are the most important. The 3-year industrial development of the process resulted in widely varying methods of handling and storing ammoniated goods, which brought about correspondingly discordant results. A final note of uncertainty was added by the proposed change in analytical control method. It was not known whether the limiting factor of ammonia addition would remain the reversion of phosphate or would become a mechanical problem incidental to the introduction of larger amounts of ammonia.

The first requisite in obtaining information on these problems was small-scale, controlled, storage equipment which could duplicate factory conditions and at the same time accelerate the reactions. This apparatus was developed.

Two major series of experiments were made, one using ammoniated superphosphate alone and the other a 4-8-4 mixed fertilizer in which the superphosphate was ammoniated to compositions corresponding to the unmixed samples. The procedure involved ammoniation of a 50-pound batch of material and immediate placing of 4 to 6 one-pound samples in the storage equipment. The samples were removed individually at the desired time intervals and analyzed. Most of the 50-pound batch was cooled, bagged in ordinary fertilizer bags, and stored in a relatively open shed. Samples of the cooled material, as well as that from the storage apparatus, were analyzed again at intervals of about 2 months to determine the stability of the products. The storage tests were made over periods of from 1 to 30 days at 60° C. and 80° C. with ammoniated superphosphate containing between 2.5 and 5.5 per cent N.

The official methods of analysis consist essentially in extracting a water-washed 2-gram sample of superphosphate with 100 cc. of neutral ammonium citrate at 65° C. for 30 minutes. The proposed method requires the use of a 1-gram sample and extraction with neutral citrate for 1 hour at 65° C. All the experimental batches were analyzed by both methods.

The factory operating problems in connection with higher ammoniation were found by experiments in several typical fertilizer mixing plants. The fine coöperation and free exchange of information between the fertilizer industry and industrial, state, and federal research laboratories have been primarily responsible for the rapid and successful growth of the ammoniation process.

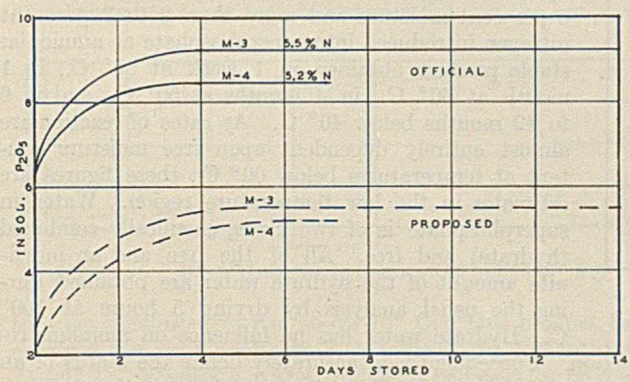

FIGURE 1. SUPERPHOSPHATE STORED AT 80° C. (176° F.)

STORAGE TESTING EQUIPMENT

Anhydrous ammonia was added to the fertilizer materials in a small drum mixer which had been used for the past $2^1/_2$ years in the experimental work. The storage tests were made in an apparatus similar to that described by Schucht (*13*), consisting of an oil-filled thermostat and several containers. The containers were short sections of a 4-inch iron pipe with a head welded in one end and fitted with a removable piston. The piston was a section of smaller iron pipe with welded oversize head fitting close to the 4-inch container. A 1- or 2-pound sample of fertilizer was introduced in the container placed upright in the oil bath. The piston was inserted and putty was pushed into the annular space between piston and cylinder walls to prevent loss of moisture from the sample. From 3 to 4 pounds pressure per square inch was applied to the piston in most of the tests by merely placing bags of lead shot on top of it. In a few cases 15 to 20 pounds per square inch was obtained by hanging the shot bags from the end of a 3-foot horizontal bar passing across the top of the piston. Increasing the pressure beyond about 3 pounds did not significantly affect the reaction.

MATERIALS

The same commercial source of superphosphate was used for the entire 6 months of the tests and the four shipments of superphosphate involved closely approximated the following average analyses: moisture, 7–8 per cent; total P_2O_5, 18.7 per cent; insoluble P_2O_5, 0.25 per cent; free acid, 3–4 per cent. The potassium chloride and sulfate of ammonia used in the 4-8-4 mixture were obtained from stock piles in a fertilizer mixing plant. No organic nitrogenous material was used in the mixtures, as previous experiments had shown this to have no specific influence on the ammoniation reaction.

The 4-8-4 mixtures were made on the basis of 4 per cent nitrogen. Typical formulas were: 4-8-4 (4.5 per cent N Super)—22.5 pounds super; 5 pounds ammonium sulfate; 4 pounds potassium chloride; 17 pounds sand; 1.1 pounds anhydrous ammonia. 4-8-4 (3 per cent N Super)—22.5 pounds super; 6 pounds ammonium sulfate; 4 pounds potassium chloride; 17 pounds sand; 0.8 pound anhydrous ammonia. Duplicate batches were made of practically all series to avoid freak data and minimize sampling and analytical errors.

FACTORY EXPERIMENTS

Early in the development of ammoniation it was realized that the addition of ammonia to superphosphate must be carried out in the present plant equipment with very little additional capital expenditure and with no decrease in the hourly production. Experiments were recently made in five widely separated fertilizer mixing plants to determine the maximum amount of anhydrous ammonia that could be mechanically introduced under the above criteria. Small-scale experiments had shown (*6*) that the chemical absorption limit was 5 to 5.5 per cent nitrogen, but it required 5 to 8 minutes in a relatively tightly enclosed mixer for complete absorption of the maximum quantity using anhydrous ammonia. The use of an aqueous solution such as ordinary aqua ammonia (25–30 per cent NH_3) made it possible to add an equivalent amount of ammonia in a shorter time, but the water so introduced caused excessive dampness in the mixture when more than about 2.5 per cent N was so added to the superphosphate. Increasing the ammonia concentration of such solutions, of course, obviates this difficulty, but more than 35 per cent NH_3 concentration produces pressures which demand the same type of equipment as anhydrous (100 per cent) ammonia. As the reversion of phosphate has been found to be practically independent of the moisture content of the goods as long as it lies in the region of 6 per cent water or above, the limit of ammoniation with concentrated ammonia solutions is on the same basis as anhydrous ammonia (reversion of P_2O_5).

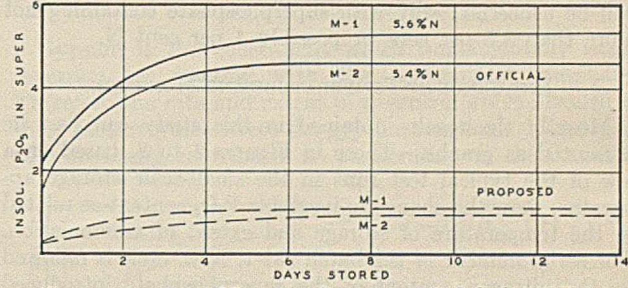

FIGURE 2. 4-8-4 MIXTURE STORED AT 80° C. (176° F.)

The factory tests included mixed goods and cured and fresh superphosphates from Tennessee and Florida rock sources. The mixers were ordinary rotary batch machines of the Sturtevant or Stedman type. It was found that 3.5 per cent N (4.25 per cent NH_3) was an average maximum limit of ammoniation with anhydrous ammonia. The limit is sharply defined for a given material and attempts to introduce more than this amount of ammonia within a reasonable time (3 to 4 minutes) resulted in excessive losses. The condition of the superphosphate and the presence of other ingredients in mixtures had relatively little effect upon this limit, although it varied as much as 0.5 per cent N between different plants.

The fresh superphosphate was appreciably dried and granulated by the ammonia treatment. Although interesting possibilities of development along this line were indicated, addition of ammonia stopped the action of the free acid resulting in a phosphate availability somewhat lower than that from cured super. The highly ammoniated mixed goods were comparable to present ammoniated materials in physical characteristics, but with even less tendency to cake and generally drier condition.

A recording thermometer buried in the pile of highly ammoniated goods showed a tendency in mixed goods to rise 2° to 4° C. the first 24 to 36 hours in the storage pile. No such tendency was noted in straight ammoniated superphosphate. The ammoniation temperatures, using 3.5 per cent N, were on the order of 90° C. for straight superphosphate and 70° C. for mixed fertilizers. The difference in behavior previously mentioned is thought to be due to this variation in initial temperatures.

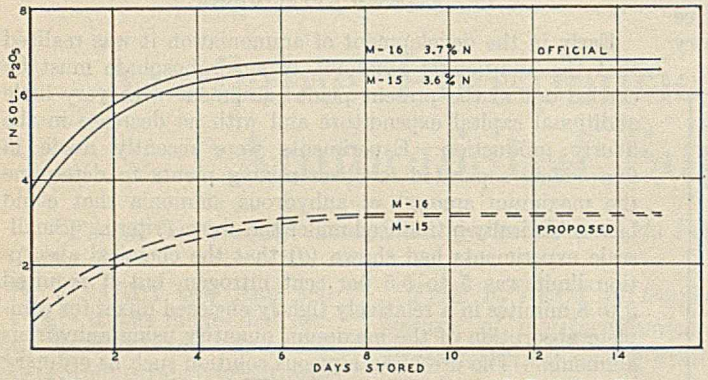

FIGURE 3. SUPERPHOSPHATE STORED AT 80° C. (176° F.)

Undoubtedly the present equipment is not the best for highly efficient ammonia absorption. However, it allows the introduction of quantities which under present price schedules and analytical methods are most advantageous. Development will occur along these mechanical lines only when more favorable conditions warrant it. Although the data here presented cover the entire range of possible ammoniation, commercial and agronomic interests at present will be concerned only with superphosphate containing not more than 3.5 per cent or possibly 4 per cent N.

INFLUENCE OF TEMPERATURE AND MOISTURE

Most of the results obtained in this study can best be presented as graphs. Those in Figures 1 to 8, based on a few of the typical test runs in the small-scale storage apparatus, show the change in insoluble P_2O_5 content as related to the temperature of storage and extent of ammoniation. The serial number of the batch (M-1, M-2, etc.) is followed by the nitrogen content of the superphosphate introduced as anhydrous ammonia. The data in all graphs are on the same superphosphate basis. All analyses of 4-8-4 mixtures were multiplied by 2.2, as only 23 pounds of the total 50-pound batch was superphosphate.

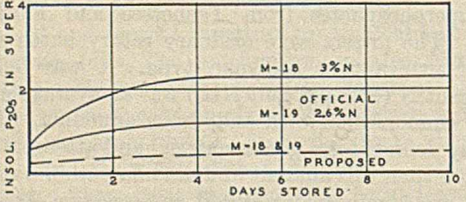

FIGURE 4. 4-8-4 MIXTURE STORED AT 80° C. (176° F.)

The difference in rate of increase in insoluble P_2O_5 at 80° and 60° C. is obvious from a comparison of Figures 1 to 8. The change in time required to reach equilibrium from 5 days at 80° C. to 28 days at 60° C. is probably entirely dependent upon temperature, as free moisture (dampness) was clearly present at each temperature. Reduction of the temperature to 40° C. or below brings in another factor—combination of free water into hydrates stable at ordinary temperature. Detailed observation of results in various fertilizer plants during the past three years has shown that final equilibrium, in goods ammoniated sufficiently to show significant reversions, was not reached for over 6 months at 25° to 30° C.

From a correlation of factory and experimental results, the following rates of reaction have been set up for average mixed fertilizers containing more than 6 per cent moisture and more than 2 to 3 per cent nitrogen introduced into superphosphate as ammonia: stable product obtained in 1 week at 80° C., in 1 month at 60° C., in 4 months at 50° C., and in 6 to 12 months below 40° C. As rates of reaction are almost entirely dependent upon free moisture content at temperatures below 60° C., these figures are estimates in the low temperature region. Water in superphosphate is of two kinds, chemically combined (hydrate) and free. All of the free and an indefinite amount of the hydrate water are obtained during the usual analysis by drying 5 hours at 100° C. Hydrate water has no influence on ammonia reaction. Consequently to accurately define the status of an ammoniated superphosphate it would be essential to know the free moisture at 25° to 30° C. Since no satisfactory method for determining this exists, arbitrary limits of total moisture (obtained at 100° C.) are the only guides to set up for control purposes.

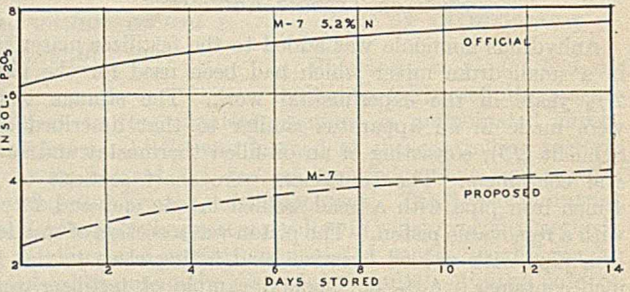

FIGURE 5. SUPERPHOSPHATE STORED AT 60° C. (140° F.)

The ratio of free to combined water depends entirely upon the temperature. Samples stored at 80° C. were always moist to the touch, even though analyses showed only 3 to 4 per cent water. Sixty-degree samples were appreciably drier but still damp, and at 40° or below the same material was dusty. This indicated hydrates ranging in stability from decomposition at 40° to 80° C. Past experience has indicated that ammoniated material containing over 6 per cent moisture is in what might be termed a normal state of hydration and also has some free water. Such a product, if highly ammoniated, will show slow reversion at 25° to 40° C. during the first 6 months. On the other hand, mixtures containing less than 6 per cent water may remain unchanged for a year at low temperatures.

From what has been said it is possible to set up certain plant operations to obtain minimum insoluble P_2O_5 with maximum ammonia absorption. As the starting points on the graphs were cooled products, it obviously is highly beneficial from the standpoint of insoluble P_2O_5 to cool ammoniated goods soon after introduction of the ammonia. The same graphs, however, just as clearly show such products to be far from equilibrium mixtures and could be compared with super-saturated solutions. Low temperature results in stability for appreciable lengths of time only if accompanied by dryness (no free moisture present). Desirability of cooling products, therefore, must be judged mainly on the probable free moisture content after cooling, if stability of product is considered.

Another factor influencing the stability of cooled goods is the initial temperature of ammoniation. During the experiments it was noticed that superphosphate ammoniated to over 5 per cent N, and thereby reaching 90–100° C., was more stable at atmospheric temperatures than material ammoniated to only 3.5 to 4 per cent in which the temperature reached only 70–80° C. To substantiate this, a batch was ammoniated to 5 per cent N in two steps and the temperature never allowed to rise above 70° C. This product lost nearly 3 per cent available P_2O_5 (official) in 4 months at 25–30° C., whereas a corresponding 5 per cent N product ammoniated at 90–100° C. lost only 0.4 per cent available P_2O_5 in the same time. Under the proposed method, the low temperature batch lost 2 per cent P_2O_5 and that at higher temperature only 0.2 per cent P_2O_5.

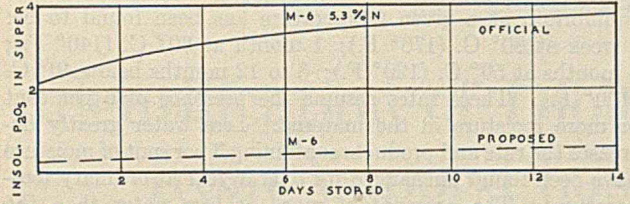

Figure 6. 4-8-4 Mixture Stored at 60° C. (140° F.)

It seems advisable, therefore, to avoid cooling during ammoniation, and even soon after, if such moisture is present. Cooling after a few days storage at elevated temperatures, piling ammoniated goods in small open piles, or anything to facilitate loss of free moisture and cooling, however, probably would delay the reversion reactions at least 6 to 8 months. Centers of large warm storage piles containing enough ammonia to cause reversion show higher reversions than the surfaces of the same piles after a few weeks, but the surface material after a year would probably be identical with the center.

Influence of Grade of Mixtures

The grade of mixture (ratio of superphosphate to total weight) has practically nothing to do with the rate and extent of reversion, except that low-grade mixtures have lower temperatures for a given degree of ammoniation and less temperature effects will be noticed. The influence of grade upon the analytical factor, however, is extremely important. It has been established that the insoluble P_2O_5 found in an ammoniated superphosphate is directly proportional to the ratio between weight of superphosphate in the sample and volume of citrate solution. The use of a constant-size sample for all mixtures containing from 8 to 16 per cent P_2O_5 inherently alters this ratio and results in different values for insoluble P_2O_5 in the same superphosphate.

Figures 9 and 10 present the necessary data for predicting the insoluble P_2O_5 in any mixture that contains only ammoniated superphosphate as the source of P_2O_5. They also show that it is possible to add more ammonia per pound of superphosphate in low-grade goods than in high grades, owing to the analytical factors mentioned. For example, in Figure 9 a superphosphate ammoniated to 3.5 per cent N and stored hot for a week or two would show 5.4 per cent insoluble P_2O_5 under present official methods of analysis. If this ammoniated superphosphate were cooled soon after making, it would contain only 3.4 per cent insoluble P_2O_5. Such a product mixed to a 4-8-4 grade or a 4-8-4 mixture ammoniated to a corresponding degree would show after long storage 2.7 per cent insoluble P_2O_5 in the superphosphate, or if cooled about 1.0 per cent. All cooled materials, indicated on the graphs by dotted lines, represent the minimum insoluble P_2O_5 that could normally be obtained. The heavy lines signify equilibrium products after long low temperature storage (below 40° C.) or short high temperature storage (above 60° C.).

The practical application of the graphs in Figures 9 and 10 should be carried out with the following factors in mind. Small piles of material (under 500 tons) would probably approach the classification "cooled." Large piles (over 500 tons) would, at least below the surface, fall into the classification of "stored hot." Moist goods (over 6 per cent H_2O) would also approach "stored hot" data rather than "cooled," because cooled moist material will show gradual reversion the first 6 months. The probable time of analysis must also be considered. Goods over 6 or 8 months old would show similar reversions, regardless of size of piles or storage temperatures unless the material was especially dry.

The vertical line at 3.5 per cent N, besides serving as an example of a selected composition, divides the practical from the theoretical areas. As already shown, 3.5 per cent N is the maximum mechanical limit of ammonia absorption with anhydrous ammonia in present plant equipment. Because of economic as well as mechanical factors, therefore, it will probably be several years before material ammoniated to the area in the right of the line (about 3.5 per cent N) will be a common article of commerce.

Chemical Reactions

Briefly, the ammoniation reactions, discussed in detail elsewhere (*6*), were:

$$CaH_4(PO_4)_2 + NH_3 = CaHPO_4 + NH_4H_2PO_4 \quad (1)$$

$$2CaHPO_4 + CaSO_4{\cdot}2H_2O + 2NH_3 = Ca_3(PO_4)_2 + (NH_4)_2SO_4 + 2H_2O \quad (2)$$

$$NH_4H_2PO_4 + CaSO_4{\cdot}2H_2O + NH_3 = CaHPO_4 + (NH_4)_2SO_4 + 2H_2O \quad (3)$$

Gypsum is the constituent which fundamentally causes reversion by reacting with the ammonium phosphates. Therefore the rate and extent of reversion are controlled by those factors which affect the gypsum reactions. Free moisture obviously contributes an acceleration to the reactions, as it enables more extensive solution of the gypsum. Furthermore, its presence decreases the stability of the ammonium phosphates. Elevated temperature, in addition to furnishing more free moisture through hydrate decomposition, increases the solubility of gypsum and greatly increases the rate of ammonium phosphate decomposition.

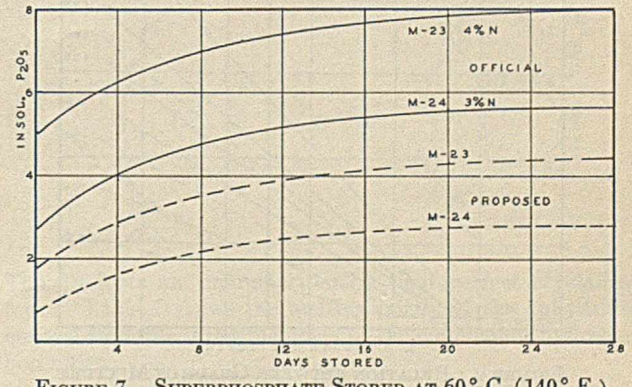

Figure 7. Superphosphate Stored at 60° C. (140° F.)

A superphosphate ammoniated at temperatures below 70° to 80° C. will contain most of its ammonia as phosphate compounds and the gypsum is only slightly involved. Consequently this product cooled will not be stable in the presence of free moisture and will show gradual reversion. The other extreme, a product ammoniated at 100° C., will have undergone probably 50 per cent of the potential gypsum reactions within an hour or less. This product when cooled is much nearer the final equilibrium point. Hence the driving force of the reactions is less and a comparatively stable product results.

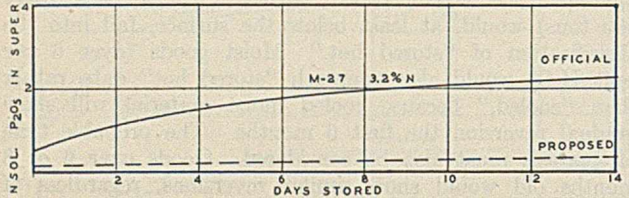

FIGURE 8. 4-8-4 MIXTURE STORED AT 60° C. (140° F.)

The fact that gypsum is of fundamental importance in the reversion reactions was again checked by storing ammoniated triple superphosphate (product from phosphoric acid and phosphate rock) at 80° C. for a week. Triple superphosphate ammoniated to 6.0 per cent N changed in insoluble P_2O_5 from 2.9 to 4 per cent, whereas a similar ratio of ammonia to calcium phosphate in ordinary superphosphate would have shown a change of from 6 to 9 per cent insoluble P_2O_5.

SUMMARY

The relationship between degree of ammoniation and reversion of P_2O_5 in superphosphate fertilizers has been determined according to the present official and proposed method of analysis. The influence of time and temperature of storage, of the presence of ordinary ingredients in complete fertilizer mixtures, of moisture content, of physical conditions, etc., upon this relationship has been investigated.

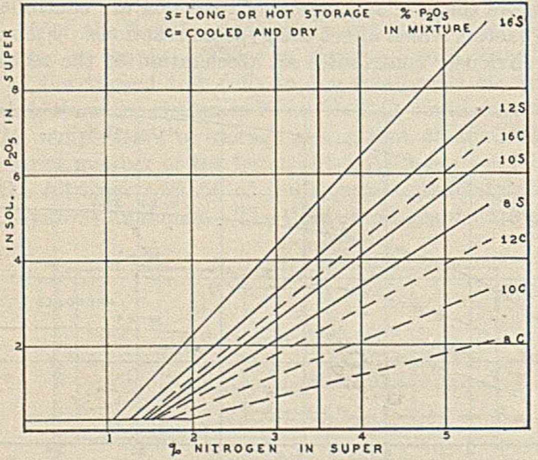

FIGURE 9. RELATION BETWEEN GRADE OF MIXTURE AND INSOLUBLE P_2O_5 (OFFICIAL ANALYTICAL METHOD)

It was established and verified by industrial results during the past two years that 30 pounds of anhydrous ammonia was the maximum that could be added to a ton of mixed fertilizer (8–10 per cent P_2O_5 grade) without encountering excessive reversion of phosphate under official analytical control. This meant that 2 to 2.5 per cent of nitrogen added as ammonia to the superphosphate in such mixtures caused a reversion of approximately 0.5 per cent P_2O_5.

The data in this paper indicate that under the proposed analytical methods 40 to 45 pounds of anhydrous ammonia can be added to a ton of mixed fertilizer (8–10 per cent P_2O_5 grade) with not more than 0.5 per cent reversion of P_2O_5. This is 3 to 3.5 per cent nitrogen added to the superphosphate.

Factory tests have also shown that mechanically 40 to 45 pounds of ammonia is the practical limit using present machinery and methods of handling in the average fertilizer factory. The rate of ammonia absorption beyond this amount is greatly reduced, with consequent decreased tonnage production per hour.

The time for an ammoniated superphosphate to reach equilibrium at a given temperature has been found to be: 1 week at 80° C. (176° F.); 1 month at 60° C. (140° F.); 4 months at 50° C. (120° F.); 6 to 12 months below 40° C. (100° F.). These rates assume the presence of 6 per cent or more moisture in the material. Less water greatly decreases the rate and products containing 3 per cent of moisture have been found unchanged for over a year at ordinary temperatures. The presence of more or less water than the average 6 to 7 per cent apparently influences the rate of reaction (reversion) but not the extent. This point is being further investigated.

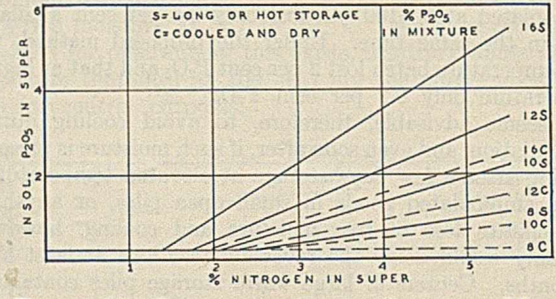

FIGURE 10. RELATION BETWEEN GRADE OF MIXTURE AND INSOLUBLE P_2O_5 (PROPOSED ANALYTICAL METHOD)

The stability of products cooled immediately after ammoniation has been found to be dependent upon (1) the initial temperature or ammoniation temperature, and (2) the presence of free moisture (as distinct from hydrate moisture). Cooling material initially over 80° to 90° C. with a moisture content less than 6 per cent results in a product apparently stable for over 6 months. If the moisture content is more than 6 per cent, reversion will occur within 6 months. Products with average moisture content (6–8 per cent H_2O), ammoniated at temperatures below 70° to 80° C. and cooled suddenly, show reversion within three or four months. After storage for a week at temperatures above 70° C. subsequent cooling, it is thought, will result in a product stable for an indefinite period.

The insoluble P_2O_5 in ammoniated superphosphate mixed to any grade of mixed fertilizer (8–16 per cent P_2O_5) can be estimated from graphs in Figures 9 and 10. The "stored" condition in these graphs represents maximum and the "cooled" designates the minimum soluble P_2O_5. The history of the sample being considered will determine to which class it belongs.

The application of the chemical equations previously worked out (*6*) to new data has been discussed.

The physical condition of superphosphate is still further improved with the application of 4 per cent or more nitrogen as anhydrous ammonia over that obtained using 2 per cent nitrogen. Less caking is found, apparently owing to vaporization of more water from the surface of the particles in the hot, highly ammoniated materials.

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Identification of Diolefins in Lower Fractions from Vapor-Phase Cracked Gasoline

S. F. BIRCH AND W. D. SCOTT, *Anglo-Persian Oil Co., Ltd., Meadhurst Laboratories, Sunbury-on-Thames, England*

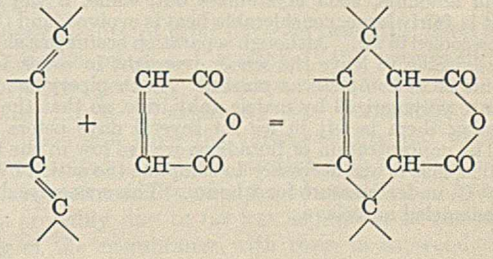
THE diolefin content of cracked distillates, even of those produced by high-temperature cracking, is generally so small that identification of individual diolefins can be accomplished only after careful fractionation by special methods. The method generally adopted for the separation of the lower members has been the addition of bromine, followed by the separation of the tetrabromides from admixed dibromides derived from the olefins. Thus butadiene and piperylene were isolated from oil-gas condensate in this way by Armstrong and Miller (*1*) while Brame and Hunter (*2*) similarly identified piperylene in the fraction boiling between 42–47° C. from cracked Russian kerosene (Cross plant). The method has the advantage that the original hydrocarbon can readily be regenerated from the solid tetrabromide by treatment with zinc dust in alcoholic solution, as well as from the accompanying isomeric liquid tetrabromide. Unfortunately, although this method of identification is perfectly satisfactory for butadiene and piperylene, both of which form easily crystallizable tetrabromides, it is useless for isoprene, cyclopentadiene, and the dimethyl butadienes, all of which give liquid tetrabromides. No doubt, by fractionating the mixed di- and tetrabromides obtained by brominating a narrow-cut gasoline fraction and by treating the high-boiling portion containing the tetrabromides with zinc dust in alcohol, it would be possible to concentrate the diolefins present, but some means of identifying them would still be necessary.

PREVIOUS WORK

Ostromisslenskii (*9*) succeeded in estimating the isoprene present in a mixture of butenes, pentenes, and benzene by shaking with concentrated hydrochloric acid for 6 hours and fractionating the carefully washed and dried product. The isoprene content was determined from the weight of the fraction boiling from 130–140° C., which was $\beta\delta$ dichlor-β-methylbutane in a fairly pure condition. While this method would no doubt give satisfactory results if the isoprene content were comparatively high, it would be useless for the pentene fraction from the average cracked gasoline. Furthermore, it again does not provide a method of identification.

Cyclopentadiene was isolated from oil-gas condensate by Etard and Lambert (*6*); their method depended upon separating the dicyclopentadiene, formed on standing, by fractionation. Cyclopentadiene has also been isolated from coke-oven benzene and from the benzene produced on the distillation of lignite (*8*). This method of isolation involving polymerization followed by depolymerization is very convenient for separating and preparing cyclopentadiene free from other hydrocarbons, but it does not afford a very good method of identification when only traces are present.

Recently it has been shown that the conjugated hydrocarbons can be estimated quantitatively by a very simple reaction. It has long been known that quinones, azo esters, and various unsaturated aldehydes react with conjugated hydrocarbons with the formation of various ring compounds. Diels and Alder (*3*) describe the preparation of acid anhydrides by the addition of maleic anhydride to conjugated hydrocarbons [see also Farmer and Warren (*7*) and Diels and Alder (*4*)]. Most of these addition products are formed with the greatest ease, generally by allowing the diolefin and maleic anhydride to react in benzene solution at ordinary temperatures. The reaction which involves the addition of one molecule of the diolefin to one of the maleic anhydride can be expressed as follows:



The products are characterized by their perfect crystalline form. Table I shows the melting points of the anhydrides derived from the lower members of the conjugated hydrocarbon series.

TABLE I. MELTING POINTS OF ANHYDRIDES

DIOLEFIN	MELTING POINT Anhydride	 Acid
	° C.	° C.
Butadiene	103–104	166
Isoprene	63–64	. . .
Piperylene	62	. . .
Cyclopentadiene	164–165	177–179
Δ^{13} Cyclohexadiene	147	Not affected by boiling water

The anhydrides and acids have been isolated for each of the dimethylbutadienes by Diels and Alder (*5*).

The ready formation of these anhydrides appeared to give an excellent method for identifying diolefins and possibly even for estimating them in cracked distillates.[1] The quantitative estimation appears to be possible for the cyclic hydrocarbons which react with maleic anhydride instantaneously with evolution of heat, but the addition with the straight-chain diolefins is a slower process. Butadiene, isoprene, and piperylene all react slowly in the cold, but the maleic anhydride appears to act as a catalyst for the polymerization of isoprene and piperylene, small amounts of a rubber-like polymer always being formed. The same phenomenon has been observed with several of the dimethylbutadienes, certain of these giving good yields of the addition product, while others give large amounts of polymer (αα dimethylbutadiene gives only polymerized products according to a private communication from F. L. Warren).

LOWER FRACTIONS

The examination of the lower fractions of comparatively close boiling range, derived from the compression gasoline from a high-temperature cracking unit and the corresponding gasoline itself (yellow naphtha), showed that butadiene, piperylene, isoprene, and cyclopentadiene were all present and easily separated. Preliminary attempts to isolate the corresponding derivatives derived from the dimethylbutadiene fraction have, however, so far been unsuccessful, probably owing to the complex nature of the fractions examined. The ease with which the cyclopentadiene derivative separates is remarkable; in fact, so great is the heat of formation that, unless the fraction is carefully cooled after the addition of the maleic anhydride, boiling takes place. The procedure adopted was as follows:

The fraction boiling over a 4° C. range, in which the diolefin had been concentrated by fractionation, was carefully dried with calcium chloride, filtered into a dry bottle, and cooled in ice, and several grams of finely powdered maleic anhydride were added. The quantity added is determined by the fraction under examination, but for identification purposes it is better to have an excess of the diolefin. The bottle was then closed with a rubber bung and vigorously shaken, and the anhydride slowly dissolved. The rest of the procedure then depended upon the diolefin present. The cyclopentadiene derivative, even if present in small amounts, soon crystallizes out, while, if the quantity present is fairly large, considerable heat is evolved, and the bottle must be cooled in ice. Although separation occurs in a short time, it is advisable to leave the whole overnight in order to ensure that this is as complete as possible. Both piperylene and isoprene are polymerized by maleic anhydride, so that the fraction containing them is left in ice for several days before working up. The concentration of butadiene was so low in the fractions examined that it was necessary to complete the action by heating to 100° C. under pressure for 8 hours. This was carried out in a small enameled autoclave.

The cyclopentadiene derivative, cis-endomethylene-3,6-tetrahydrophthalic anhydride,[2] was very insoluble and was easily filtered off. It chiefly occurred in the fraction boiling from 40–44° C. After recrystallization from petroleum ether, it melted at 164° C., and mixing with an authentic specimen did not lower this melting point. (Analysis gave 65.76 per cent carbon and 4.82 per cent hydrogen; $C_9H_8O_3$ requires 65.85 per cent carbon and 4.88 per cent hydrogen.)

Cyclopentadiene was also obtained when the high-boiling residue, obtained on distillation of the compression gasoline, was fractionated, and the fraction boiling between 60° and 80° C. at 25 mm. pressure, which possessed a strong odor of dicyclopentadiene, slowly distilled over iron filings. The cyclopentadiene in the distillate was identified by means of the maleic anhydride condensation compound.

The piperylene derivative, cis-6-methyl-Δ^4-tetrahydrophthalic anhydride, occurred in the same fraction as the cyclopentadiene but could only be isolated by evaporation of the residual hydrocarbons. The addition product then crystallized out and was purified by recrystallization from benzene and petroleum ether (boiling point 60–80° C.); it melted at 62° C., and a mixed melt with an authentic specimen showed no depression. (Analysis gave 65.0 per cent carbon and 5.86 per cent hydrogen; $C_9H_{10}O_3$ requires 65.06 per cent carbon and 6.02 per cent hydrogen.) The isoprene derivative, cis-5-methyl-Δ^4-tetrahydrophthalic anhydride was isolated in a similar manner from the fraction boiling between 33° and 37° C.; it melted at 64° C. There was no depression of the melting point when admixed with a genuine specimen. (Analysis gave 65.01 per cent carbon and 6.00 per cent hydrogen; $C_9H_{10}O_3$ requires 65.06 per cent carbon and 6.02 per cent hydrogen.)

The butadiene addition product, cis-Δ^4-tetrahydrophthalic anhydride, was obtained by heating the gasoline fraction boiling below 20° C., consisting mainly of butanes and butenes, with maleic anhydride for 8 hours in a small enameled autoclave at 100° C. A quantity of rubber-like polymer was formed at the same time, from which the butadiene derivative was freed by crystallization from benzene and petroleum ether (boiling point 60–80° C.). The impure anhydride melted at 88° C., but after two recrystallizations the melting point rose to the correct temperature, 104° C. The pure material did not depress the melting point of a genuine specimen. (Analysis gave 63.12 per cent carbon and 5.22 per cent hydrogen; $C_8H_8O_3$ requires 63.02 per cent carbon and 5.26 per cent hydrogen.)

The viscous oil, which remained after all the hydrocarbon and solid material had been removed from the treated cyclopentadiene-piperylene fraction, very slowly deposited further crystals of the cyclopentadiene derivative upon long standing. The oil left when these crystals had been removed by filtration was distilled under reduced pressure. Practically the whole passed over between 138° and 142° C. at 3 mm. pressure. The distillate on hydrolysis gave an acid which would not crystallize. Upon standing for several months, a further quantity of the cyclopentadiene derivative separated from the distillate, but the main portion could not be induced to solidify. Analysis showed that it was probably a mixture of the anhydrides derived from piperylene and isoprene. Its chief interest lay in the ease with which it distilled, indicating thereby a possible method for separating the liquid anhydrides obtained by the treatment of the higher fractions now awaiting investigation.

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[1] Recently a patent taken out by the I. G. Farbenindustrie A.-G., British Patent 352,164 (July 9, 1931), claims the use of maleic acid or its anhydride for the purification of crude benzene from coke ovens or gas plants. The treatment as described is carried out by adding from 0.3–10 per cent (generally 1–3 per cent will suffice) to the crude benzene and, after refluxing for 2 hours, distilling off the purified material. It is suggested that the residue, which contains methylene tetrahydrophthalic anhydride may prove useful for the preparation of resin esters.

[2] This constitution was suggested by Diels and Alder (*3*), but Farmer and Warren (*7*) have been unable to confirm this structure.

Effect of Chemical Treatment on Wood Permeability

Alfred J. Stamm, *Forest Products Laboratory, Madison, Wis.*

DOUGLAS FIR specimens 1 foot (30.48 cm.) long and thin Sitka spruce sections were treated with chlorine gas, followed in some instances by a treatment with ammonia gas or ammonia water. Permeability measurements, using the previously developed differential pressure-drop hydrostatic-flow apparatus, and measurements of the effective opening diameters, using the method for overcoming the effect of surface tension, show that the treatment opens the capillary structure, presumably as a result of solvent action on the lignin of the pit membranes that constitute the major resistance to flow. Permeability increases ranging from twofold to one hundred and thirty fold were obtained under varying conditions.

ONE of the primary objects in developing the previously reported physical methods for studying the capillary structure of wood (*4*, *5*, *6*, *7*, *8*) has been to obtain a means of quantitatively investigating the effect of chemical and physical treatment on its permeability. Data obtained from such measurements should be of value in developing means of increasing the permeability, which, in turn, might be of value in the impregnation of resistant woods with preservatives and in the impregnation of chips with chemicals in chemical pulping processes.

RELATED INVESTIGATIONS

Other investigators have become interested in the same problem. Johnson and Maass (*1*) found that treatment with pulping liquors in general increases the subsequent permeability of wood to water. Scarth and Spier (*3*), measuring the permeability of wood, found that untreated heartwood sections of red spruce (it was not stated whether these were seasoned or unseasoned) gave a flow of only 1 cc. of water in 22 hours, under the conditions selected. When the sections were boiled in water the permeability increased, the flow becoming 20 cc. for the same length of time. Treatment with lignin solvents gave a flow of 10 to 80 cc. in the same time. These investigators state that the increase in rate of flow caused by boiling the wood in water is due to the removal of hemicelluloses. This, however, seems highly improbable. Even with unseasoned wood, in which the air content is relatively small, it is still sufficient to affect the permeability markedly (*5*, *6*). The boiling process, which removes a large percentage of the residual air, can readily account for the twenty fold increase in permeability. The rates of flow obtained with the chemically-treated sections, from which some air undoubtedly is removed during treatment, should be compared with the rate of flow obtained with the water-boiled specimens rather than with the unboiled. The largest increase in permeability obtained on this basis with the lignin solvents used was about fourfold. As different amounts of air may be removed in different solvents, quantitative comparisons of the increase in permeability are impossible.

Neither the simple experimental method used by Scarth and Spier nor the much more complicated method of Johnson and Maass, which was designed to duplicate as nearly as possible commercial pulping conditions, is adequate for obtaining data that can be used in calculating the dimensions of the effective capillaries and the changes in these dimensions. Such measurements can be made, however, by using methods previously reported (*5*, *6*, *7*, *8*).

This paper, supplementing earlier ones, is a preliminary report in which the possibilities of increasing the permeability of wood are demonstrated and some of the theoretical inferences are pointed out.

FINE CAPILLARY STRUCTURE OF WOOD

A brief description of the fine capillary structure of wood will help toward an understanding of the effect of chemical treatment on permeability.

The fiber cavities that make up the major part of the void volume of wood are closed at both ends, the only communication from fiber cavity to fiber cavity being through the pores in the membranes of the bordered pits. It is the size, as well as the number, of these fine openings in the pit membranes that controls the permeability of wood to hydrostatic flow. Each softwood fiber with an average length of about 0.3 cm. and a diameter of approximately 0.003 cm. has from 30 to 300 pits connecting it with adjoining fibers, and there are from 50,000 to 100,000 such fibers in a square centimeter of cross section.

Figure 1 shows a photomicrographic section of a typical softwood cut across the fibers. A bordered pit connecting two adjacent fiber cavities is shown in cross section. The openings in the adjacent cell walls, which are almost circular, are separated by a membrane that is a continuation of the middle lamella, the cementing material between the fibers. The pit membranes, particularly those of softwoods, have a slight central thickening called the torus. Sometimes the pits are aspirated, that is, the torus is held against one of the seats of the cell wall opening, making the pit act like a closed valve.

The permeability of a pit depends primarily upon its condition. If the pit is not aspirated, the permeability is a function of the porosity, the area, and the thickness of the membrane. If it is aspirated, the permeability further depends upon how close the valve seat fits and whether or not it is cemented in a closed position with resinous material. The greater permeability of sapwood over that of heartwood (*7*, *8*) is probably due to far less aspiration of the pits and clogging of the membranes with resin in sapwood than in heartwood.

EXPERIMENTAL PROCEDURE AND RESULTS

The fact that practically the entire resistance to the flow of liquids through wood is in the pit membranes, which are composed of lignin (*2*), immediately suggests that the permeability of wood might be increased through the use of lignin solvents. Since it would be commercially desirable to increase the permeability of resistant woods only, it is important to use a means of solvent treatment that is as effective as possible in completely penetrating the wood.

A gaseous treatment of the partially seasoned wood seemed the most promising method. Chlorine reacts with lignin to form a compound that is soluble in dilute alkali or ammonium hydroxide. The procedure adopted was to pass chlorine gas, which had been humidified by bubbling through water, longitudinally through the specimen. Glass adapters with hard rubber flanges for clamping to the ends of the specimen served to conduct the gas. The discharge tube was dipped into a beaker of oil so that the rate of passage of the gas could be observed from the rate of bubbling. With the type of connection used, leakage made it impossible to apply chlorine pressures greater than a few atmospheres. Improvement of the clamping device may permit greater pressures. The chlorine-gas treatment was in some cases followed by a similar treatment with ammonia gas and this, in turn, by a treatment with steam.

Measurements were first made upon transverse sections of Sitka spruce 1 to 2 cm. thick (3 to 6 fiber lengths). The chlorine and the ammonia gas passed through these sections readily and uniformly. The uniformity of the coloration of the wood (orange from the chlorine and black from the ammonia) made the uniformity of the penetration evident. Little radial or tangential penetration of the gas occurred, the colored discharge surface having practically the same dimensions as the intake surface. After treatment for the periods indicated in column 2 of Table I, the sections were soaked in distilled water for 2 weeks, with frequent changes of the water. To facilitate the replacement of air by water the soaking was done in a vacuum desiccator to which suction was applied intermittently. Measurements of the permeability were then made, using the previously developed differential pressure-drop hydrostatic-flow apparatus (*5*, *6*, *7*), and of the maximum effective opening diameter, using the method for overcoming the effect of surface tension (*5*, *6*).

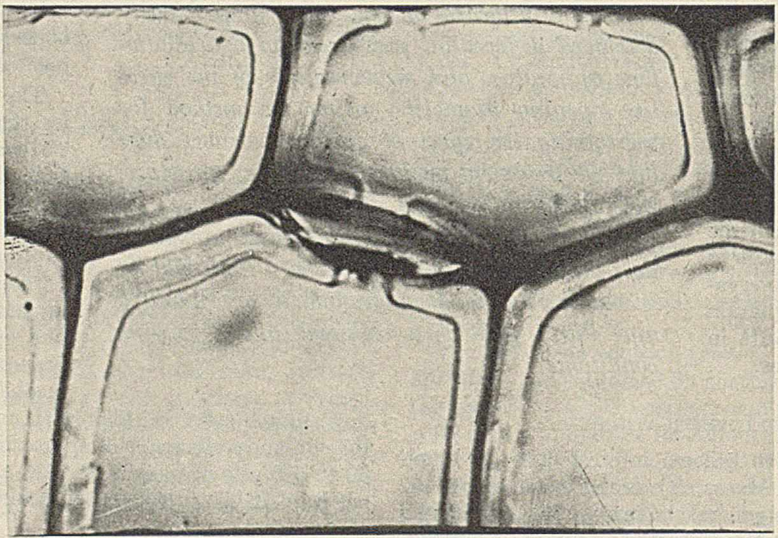

FIGURE 1. CROSS SECTION OF SOFTWOOD. Aspirated bordered pit connecting two adjacent fiber cavities (× 2000) is shown.

Table I shows the results of measurements on thin, treated, transverse sections of Sitka spruce. The 2-hour chlorine treatment caused a considerable increase in the permeability and in the maximum effective capillary radius, while the shearing strength of the section seemed to be only slightly reduced. With the prolonged chlorine treatment, followed by a treatment with ammonia gas, the permeability and the maximum effective radius were further increased, but the shearing strength was enormously reduced.

Table II gives the results from a longitudinal treatment of specimens of Coast Douglas fir 1 foot (30.48 cm.) long. After the treatment test sections were cut from the ends and center of the specimens. These were soaked in distilled water and subjected to the same vacuum treatment as the Sitka spruce sections. The results for specimen 3 show that a physical pressure treatment of the partially soaked specimen in an autoclave has no effect upon the permeability. Building up the pressure to 5 kilograms per square centimeter and suddenly releasing it does not cause rupture of the pit membranes, as is made evident by the fact that the permeability and the maximum effective radii remain unchanged. Further attempts to cause rupture of the pit membranes mechanically will be made, using high pressures, freezing, and perhaps a combination of freezing and high pressure.

Chlorine treatment of the long specimens of Douglas fir, followed by soaking in ammonia water, was less effective in uniformly opening the structure than it was with the thin Sitka spruce sections. The permeability increase for the center section was appreciably less than that for the section cut from the intake end, showing that the effectiveness of the treatment falls off toward the middle of the specimen. When ammonia gas was passed through the specimen, instead of soaking it in ammonia water, the opening of the capillary structure was more nearly complete throughout the specimen. With both forms of treatment, radial penetration and tangential penetration were negligible. Longitudinal penetration was far less uniform over the cross section of the specimen than for the thin Sitka spruce sections. The specimen treated by soaking in chlorine water, instead of being subjected to the gas, showed a smaller increase in permeability and in the maximum effective capillary radius, which diminished even more toward the middle of the specimen than with specimen 3. This should be expected, as the penetration of chlorine water was not greater than 1/8 inch (0.32 cm.) radially and tangentially and was far from uniform longitudinally. Treatment of unseasoned wood in this manner might have been much more effective, as the chlorine could then diffuse quite readily through the sap.

The maximum effective capillary radii presented in both Table I and Table II, in general, show a decrease in the effective radius with an increase in thickness of the test section (*7*, *8*). This is due to the fact that the effective path through a number of pit membranes in series will approach an average value as the number increases, because of the decreasing probability that all those in series contain pores of maximum size.

It is of interest to calculate what the increase in permeability would have been if the average effective capillary radii had increased at the same rate as the maximum. These values are given in Table III. The calculated permeability increase for the thin Sitka spruce specimens does not greatly exceed the observed permeability, showing that the average effective capillary radii increase almost at the same rate as the maximum effective capillary radii. With the longer Douglas fir specimens the calculated permeability is a number of times greater than the observed value, indicating that the greater part of the increase in the capillary radii is confined to the more effective capillary paths. The same conclusion can be drawn from the fact that the coloration of the Douglas fir specimens caused by the chlorine gas is not uniform over the operative cross section of the specimens, indicating that the penetration and subsequent chemical action followed largely the capillary paths of least resistance.

TABLE I. EFFECT OF CHEMICAL TREATMENT OF THIN TRANSVERSE SECTIONS OF SITKA SPRUCE ON PERMEABILITY TO WATER AND MAXIMUM EFFECTIVE CAPILLARY RADII[a]

SECTION	TREATMENT	EFFECT ON STRENGTH	THICKNESS OF SECTION	EXTRAPOLATED PRESSURE-DROP RATIO $\frac{P_2}{P_1}$	PERMEABILITY FOR UNIT DIMENSIONS PER CM. MERCURY PRESSURE	PRESSURE TO OVERCOME SURFACE TENSION	MAXIMUM EFFECTIVE CAPILLARY RADIUS
			Cm.		*Cc./hr.*	*Kg./cm.*^{2}	*Cm.*
1	Untreated	...	1.130	0.004	0.0172	13.0	11.3×10^{-6}
2	Untreated	...	1.885	0.0025	0.0179	17.0	8.6×10^{-6}
3	Chlorine 2 hours, steam 1/2 hour	Slight reduction	1.215	0.120	0.552	5.0	29.4×10^{-6}
4	Chlorine 2 hours, steam 1/2 hour	Slight reduction	1.800	0.075	0.512	7.0	21.0×10^{-6}
5	Chlorine 8 hours, let stand 2 days in contact with chlorine gas, steam for 1/2 hour, ammonia gas 1 hour, steam for 1/2 hour	Total destruction	1.090	0.550	2.28	3.5	42.0×10^{-6}

[a] Operative cross section of differential pressure-drop hydrostatic-flow apparatus = 2.08 cm.^{2} Standard capillary constant, $\frac{r_2^4}{l_2}$, of differential pressure-drop hydrostatic-flow apparatus = 3.73×10^{-9}.

TABLE II. EFFECT OF CHEMICAL TREATMENT OF COAST DOUGLAS FIR SPECIMENS 30.48 CM. LONG ON PERMEABILITY TO WATER AND MAXIMUM EFFECTIVE CAPILLARY RADII[a]

SPECIMEN	TREATMENT	THICKNESS OF TEST SECTION	LOCATION OF SECTION IN SPECIMEN	EXTRAPOLATED PRESSURE-DROP RATIO $\frac{P_2}{P_1}$	PERMEABILITY FOR UNIT DIMENSIONS PER CM. OF MERCURY PRESSURE	PRESSURE TO OVERCOME SURFACE TENSION	MAXIMUM EFFECTIVE CAPILLARY RADIUS
		Cm.			*Cc./hr.*	*Kg./cm.*^{2}	*Cm.*
1	Untreated	0.940		0.0034	0.0164	43.6	34×10^{-6}
	Untreated	1.362		0.0025	0.0174	59.8	25×10^{-6}
2	Untreated	0.930		0.0033	0.0157	40.0	37×10^{-6}
3	5 kg./cm.^{2} pressure applied to partially soaked specimen and suddenly released 5 times	0.975	(1) End	0.0031	0.0163	43.6	34×10^{-6}
		1.425	(2) Next to end	0.0022	0.0161	71.7	21×10^{-6}
		0.908	(3) Center	0.0037	0.0172	40.0	37×10^{-6}
		1.400	(4) Center	0.0022	0.0158	73.7	20×10^{-6}
4	Chlorine 6 hours, let stand overnight in contact with chlorine, soaked in ammonia water, and put through pressure treatment of 3	1.495	(1) Intake end	0.0155	0.1190	27.4	54×10^{-6}
		1.009	(2) Next to intake end	0.0175	0.0905	17.6	84×10^{-6}
		0.945	(3) Center	0.0155	0.0753	18.3	81×10^{-6}
		1.428	(4) Center	0.0100	0.0732	30.2	49×10^{-6}
5	Same as 4 except that ammonia was passed through specimen for 1 hour instead of soaking in ammonia water before pressure treatment	1.043	(1) Intake end	0.022	0.1180	17.6	84×10^{-6}
		1.515	(2) Next to intake end	0.014	0.1090	28.8	51×10^{-6}
		1.020	(3) Center	0.016	0.0838	21.1	70×10^{-6}
		1.450	(4) Center	0.012	0.0893	33.7	44×10^{-6}
		0.910	(5) Next to discharge end	0.018	0.0842	21.1	70×10^{-6}
		1.445	(6) Discharge end	0.012	0.0890	32.3	46×10^{-6}
6	Soaked in chlorine water for 1 week and put through pressure treatment of 3	1.445	(1) End	0.009	0.0668	37.3	40×10^{-6}
		0.980	(2) Next to end	0.012	0.0604	24.6	60×10^{-6}
		1.500	(3) Center	0.006	0.0462	42.2	35×10^{-6}
		0.975	(4) Center	0.008	0.0400	26.7	55×10^{-6}

[a] Operative cross section of differential pressure-drop hydrostatic-flow apparatus = 1.54 cm.^{2} Standard capillary constant, $\frac{r_2^4}{l_2}$ of differential pressure-drop hydrostatic-flow apparatus = 3.73×10^{-9}.

TABLE III. COMPARISON OF ACTUAL INCREASE IN PERMEABILITY WITH INCREASE EXPECTED IF AVERAGE EFFECTIVE CAPILLARY RADII INCREASED AT SAME RATE AS MAXIMA EFFECTIVE CAPILLARY RADII

WOOD SPECIES	SPECIMEN	SECTION	OBSERVED PERMEABILITY INCREASE	EFFECTIVE CAPILLARY RADIUS INCREASE	CALCULATED PERMEABILITY INCREASE	RATIO OF CALCULATED TO OBSERVED PERMEABILITY INCREASE
			Times normal	*Times normal*	*Times normal*	
Sitka spruce	...	3	32.1	2.60	46.0	1.43
Sitka spruce	...	4	28.6	2.44	35.7	1.25
Sitka spruce	...	5	132.7	3.72	191	1.44
Coast Douglas fir	4	1	7.26	2.57	43.7	6.02
		2	5.52	2.47	37.5	6.75
		3	4.59	2.38	32.3	7.03
		4	4.47	2.33	29.5	6.60
Coast Douglas fir	5	1	7.20	2.47	37.5	5.20
		2	6.65	2.43	35.0	5.27
		3	5.11	2.06	18.1	3.55
		4	5.44	2.09	19.3	3.55
		5	5.13	2.06	18.1	3.53
		6	5.43	2.19	23.1	4.25
Coast Douglas fir	6	1	4.07	1.90	13.1	3.22
		2	3.69	1.77	9.8	2.66
		3	2.82	1.75	7.8	2.76
		4	2.44	1.62	6.9	2.83

An extension of these measurements, including measurements of the ratio of the effective capillary length to the effective continuous capillary cross section, using the recently developed electrical conductivity method (*7*, *8*), is contemplated. Undoubtedly more favorable methods of treating and treating conditions can be found for opening the fine capillary structure of wood than the few methods of treatment and conditions thus far tested.

SUMMARY

Treatment with chlorine gas and treatment with chlorine gas followed by a treatment with ammonia open the fine capillary structure of wood enough to increase its permeability to water. Using a drastic treatment a permeability increase of one hundred and thirty fold was obtained with a thin section, but under such treatment the strength of the wood was almost totally destroyed. Milder treatment caused a smaller increase in permeability without greatly affecting the strength. Longitudinal treatment was found to increase the permeability several fold at a distance of 1 foot (30.48 cm.) from the treating end.

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X-Ray Study of Rubber Structure

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IT IS SHOWN by x-ray diffraction methods that a time interval is required to build up a fiber structure in stretched rubber. Four rather obvious types of explanation for this effect are pointed out, and serious objections to three of these are mentioned. The most probable explanation seems to be that time is required either to squeeze out unfavorably oriented molecules to the interfaces of fibers made up of favorably oriented molecules; or to pull out, in the direction of fiber-orientation, tangled portions of molecules. Such a picture would cause the easily stretched, favorably oriented molecules to assume the role usually played by the more solid phase of a gel, and would cause the less favorably oriented molecules (or portions of molecules) to play the part ordinarily played by the liquid phase of a gel.

SINCE the outstanding properties of rubber are those of a colloidal gel, it would seem reasonable at first sight to picture it as having the two-phase structure found for ordinary jellies. The chemical data in the literature do not seem to be in entire accord with such a simple picture, and even the published x-ray work on stretched rubber is capable of more than one simple interpretation. It has therefore seemed worth while to carry out additional x-ray experiments of a somewhat different type on the ultimate structure of rubber.

Review of Previous Work

It will facilitate the discussion of the new data presented here if the results of work so far reported in the literature are first outlined briefly. These results[1] may be classified in the following manner: the existence and mutual transformation of different polymers in rubber; and data concerning the physical structure as determined from x-ray diffraction patterns.

Existence of Polymers in Rubber. The existence of two different constituents in rubber was assumed by many of the early workers in the field. The first workers include Govi (*10*) who in 1867 assumed that rubber is analogous to a solid foam. His work was shortly disproved, however, by Thomas (*25*) and later by Hehesus (*15*). Theories based on the presence of two constituents in rubber have been set forth by many workers, including Malock (*20*), Fessenden (*7*), Breuil (*2*), Chaveau (*4*), Schwarz and Kemp (*24*), and Cheneveau and Heim (*5*). There have also been many attempts to separate the constituents of rubber. Weber (*27*) and Caspari (*3*) were the first to attempt the fractionation of rubber into hydrocarbons of different properties. This has been successfully accomplished by Duclaux (*6*), Feuchter (*8*), and Pummerer (*23*). These hydrocarbons were shown to have the empirical formula C_5H_8, but exhibited entirely different degrees of polymerization. The more soluble polymers have been designated as alpha rubber, and the more insoluble resinous forms as beta rubber. It is doubtful if any sharp dividing line can be drawn between different groups of polymers. In recent years a number of investigators, including Pickles (*22*), Lunn (*19*), Freundlich and Hauser (*9*), Van Rossem (*26*), Park (*21*), Hauser (*11*), and others, have conducted investigations on the structure of rubber, based on the properties which it would possess if it consisted of such polymers. Further experiments by Bary and Fleurent (*1*) and others have been interpreted as showing that these polymers are mutually transformable, that in ordinary rubber there is an equilibrium value for the relative amounts of the various polymers present, and that this equilibrium can be disturbed by aging, heating, etc.

From the foregoing data it will be seen that there is much evidence in favor of the existence of analogous substances in rubber whose physical properties differ to a considerable extent. For information regarding the structure of these substances in ordinary rubber, it is necessary to turn to x-ray data.

X-Ray Determinations. X-ray experiments by Katz and Bing (*16*, *17*, *18*) showed in 1925 that, when a beam of x-rays from a pinhole slit impinges on normal unstretched rubber, the only diffraction is that characteristic of amorphous substances; i. e., the diffraction pattern shows only diffuse uniform rings of low intensity. They found, however, that, when the substance was sufficiently stretched, the diffraction rings changed in intensity from point to point so that they tended to appear as small areas or "diffraction spots," thus giving diffraction patterns characteristic of fibrous materials. These diffraction spots disappear when the tension on the rubber is released, or when the rubber is heated.

Hauser and Mark (*13*) confirmed the work of Katz and Bing, and showed that excessive elongations (1000 per cent) do not change the positions of the diffraction spots but do increase their intensity. The percentage of elongation in the rubber at which the diffraction spots appear depends upon the rate of stretching (*14*). If raw rubber is stretched slowly enough, diffraction spots will not appear even at 500 per cent elongation.

Hauser and Mark at first explained these results by assuming that unstretched rubber is made up of two types of material, one of which is "dissolved" in the other. These may be thought of as being the two groups of polymers mentioned by Bary and Fleurent (*1*). It was further assumed that, in the unstretched rubber, crystalline aggregates or fibers of the higher polymers (beta rubber) exist, but that they are swollen and distorted by the presence of the lower polymers (alpha rubber) and do not therefore give rise to a diffraction pattern. By quickly stretching the rubber, however, the alpha rubber is expelled, leaving the regularly oriented cystalline aggregates of beta rubber which are responsible for the x-ray diffraction pattern.

Later Hauser (*12*) modified this theory somewhat by assuming that rubber consists of long helical parallel chains of isoprene molecules which unwind during stretching. The "coiled-spring" type of molecule would not give a diffraction pattern, but in the stretched position the symmetry would be such as to give a diffraction pattern. This theory does not necessitate the postulation of a number of polymers in rubber despite the chemical evidence, but, on the other hand, it does not require that such a postulate be abandoned. It would seem to be a corollary to such a picture that, when a strip of rubber is stretched, not only is it necessary to pull out some of the helical molecules into straight chains, but it would be necessary to push aside the other molecules to the fiber interfaces in order that the straight chains should not be warped.

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[1] Excellent reviews of the work on the composition and structure of rubber have been published by Hauser and Bary [*Rubber Age* (*N. Y.*), 23, 685–8 (1928)], and by G. L. Clark [*Indian Rubber World*, 79, 559 (1929)]. The present summary is limited to those articles which seem to have a direct bearing on the present work.

The regularly oriented straight chains would then be capable of giving rise to the observed diffraction patterns.

If this last theory is correct, it would be expected that a time interval would be required after stretching before rubber could show evidence of crystallinity. This interval would represent the time required for those molecules which were not oriented along the direction of stretch to leave the oriented fibers and travel to the fiber-boundary. It is the purpose of the present work to demonstrate the presence or absence of this time interval, thus bringing one step closer a tenable picture of the structure of rubber.

Apparatus and Experimental Procedure

Apparatus. A schematic diagram of the apparatus used is given in Figure 1.

A Coolidge x-ray tube, *A*, was used with a molybdenum target operating at a potential of 30,000 volts. After passing through the shutter system, *S* and S_1, the K-beta radiation from the molybdenum target was filtered out with a zirconium filter, *F*. The x-ray beam was further defined by the holes, S_2 and S_3, which were 1.6 mm. ($^1/_{16}$ inch) in diameter. Scattered radiation from the holes was eliminated by allowing the beam to pass through a 6.4-mm. ($^1/_4$-inch) hole in the screen S_4. The beam was diffracted by the rubber specimen, *R*, and the pattern was obtained on the film, *P*. The rubber was fastened between a fixed support, M_1, and a movable support, M_2. The latter was held under tension by the spring, *N*, and was moved up and down by the action of the cam, *C*, which had a throw of 30 mm. ($1^3/_{16}$ inches). The cam was so designed that the rubber was stretched rapidly to a position of maximum elongation and was held in this manner for one-half of a revolution of the cam, after which it was allowed to return rapidly to its original position, and the cycle was then repeated. A commutator, *O*, containing 21 segments, was mounted on the same shaft as the cam, and the two brushes, B_1 and B_2, in contact with it were mounted at 90° to each other. These brushes and the windings of an electromagnet, *E*, were connected in series through a fixed resistance, R_3, to a 110-volt source of potential as shown. By connecting together a portion of the segments of the commutator in the proper manner, the shutter, *S*, could be operated by the electromagnet in synchronism with the stretching of the rubber, so that the shutter was opened only when the rubber was in a position of maximum elongation. Also, by connecting different members of the commutator segments together, the shutter could be held open for different lengths of time, and the phase relation of this time to the stretching cycle could be controlled. The shaft on which the cam and commutator were mounted was turned by a motor, *M*, having a variable speed control, *V*. The motor was connected to the shaft through a worm and gear arrangement, G_1 and G_2, which reduced the speed of the shaft to one-fiftieth of that of the motor. The motor had a maximum speed of 1200 r. p. m., thus giving a maximum of 24 stretches of the rubber per minute. By means of the variable speed control, a minimum of approximately 4 stretches of the rubber per minute could be obtained. The variable speed control consisted of a number of lamp resistances, R_1, R_2, R_4, R_5, R_6, R_7, which could be connected in the motor circuit as shown in Figure 1.

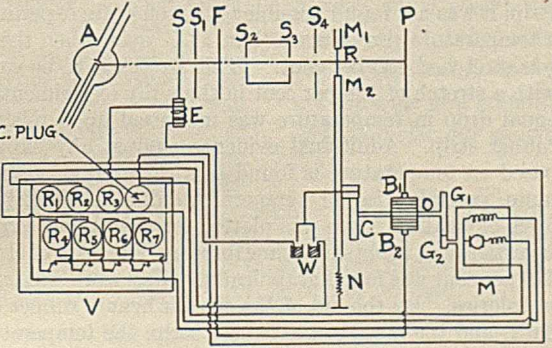

Figure 1. Schematic Diagram of Apparatus

Since previous work has shown that the intensity of the interferences is very markedly affected by the rate of stretching, it was desired to maintain a constant rate of stretching during all of the experimental work. By maintaining a constant rate of stretch, however, the time range over which the rubber could be held in a position of maximum stretch would be seriously limited. Therefore an automatic switching arrangement, *W*, was devised which consisted of a forked piece of copper fastened to the reciprocating shaft, M_2, operated by the cam, *C*, in such a way that during the period of maximum stretch it would make contact between the mercury wells indicated in Figure 1. This in turn altered the resistance in the motor circuit, thus changing the speed of the motor and hence the time of maximum stretch. The switch, *W*, slowed down the motor speed to any desired value at the instant when the rubber had reached a position of maximum stretch. This speed of the motor was held at this value so long as the cam, *C*, held the rubber in a position of maximum stretch, but at the end of this period the switch broke contact and the motor resumed its original speed. When the rubber had again reached the position of maximum stretch, the cycle was repeated.

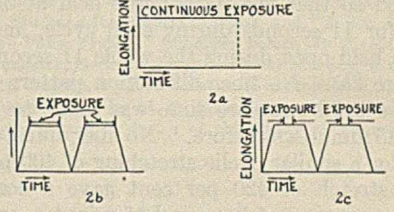

Figure 2. Graph of Stretching

Procedure. The samples of rubber used were 25 mm. long, 8 mm. wide, and 1.5 mm. thick. The ends were protected from abrasion by thin rubber facing strips, which were held in position on the sample by means of brass clamps. These clamps were attached directly to the ends of M_1 and M_2 of Figure 1. The length of the rubber strip between the clamps was kept constant. It was somewhat more than 6.4 mm.

Rapid reproducible stretching was obtained by means of the cam, *C*, of Figure 1, which was shaped so that the rate of stretching and the rate of relaxation were equal. In all of the work the time of stretching was 0.6 second. Since the amount of stretch was 30 mm. (420 per cent), the rate of stretching was approximately 50 mm. (i. e., 700 per cent) per second.

The rubber was held in a position of maximum stretch for 180° of each revolution of the cam. By means of the switch, *W*, of Figure 1 the time during which the rubber was held at maximum stretch could be varied from 1.2 seconds to approximately 11 seconds.

The total time of exposure varied with the particular kind of rubber in use and with the percentage of elongation. With the kind of rubber used in the final experiments, 1 hour and 45 minutes were found to be sufficient. Since the shutter was open only a fraction of the time in most of the experiments, the total time of the run varied in length. The exposure was made at various parts of the cycle in order to determine what the time interval was (if any) between the time of stretching and the beginning of the fiber state. This is illustrated diagrammatically in Figure 2.

A large number of preliminary experiments was made, using ordinary vulcanized "inner tube" rubber. This was found to be unsatisfactory for the present purposes, partly because of the very great elongation necessary to obtain a diffraction pattern, and partly because of the presence of diffraction spots caused by the orientation of the $MgCO_3$ used as a filler in the rubber. Pure rubber was likewise found to be unsatisfactory, owing to fatigue on continued stretching. The rubber which was used in the final experiments was vulcanized to give it the necessary toughness, but it contained only small amounts of inorganic fillers and had not been subjected to prolonged mechanical treatment, and therefore gave good diffraction patterns without excessive elongation. Its composition was as follows:

	Parts
Pale crepe	90.0
Mineral rubber	5.0
Sulfur	1.5
Accelerator	0.5
ZnO	2.5
Antioxidant	1.0

It had been milled on warm rolls for about 20 minutes.

Interpretation of Results

It was found that an elongation of 380 per cent, maintained continuously (Figure 2*a*) gave a faint fiber diffraction pattern in 1 hour and 45 minutes. Then the stretching mechanism was operated so that the rubber was held at 380 per cent elongation for 11 seconds during each cycle, and the x-ray shutter was held open during the whole 11 seconds for each cycle (Figure 2*b*). No fiber diffraction pattern was found, although the total exposure time was made to total up to 1 hour and 45 minutes as before. No fiber diffraction pattern was found for a similar cyclic stretching of 400 per cent. A continuous stretch of 420 per cent gave a comparatively strong fiber pattern, in 1 hour and 45 minutes, and a weaker fiber pattern was obtained (film 100) with a cyclic stretching of 420 per cent when the x-ray shutter was held open for 11 seconds after stretching, the total exposure time being still 1 hour and 45 minutes. Then the rubber was stretched cyclically 420 per cent, and the shutter was kept open only 1.2 seconds after the end of each stretching cycle. No certain evidence of a fiber pattern could be found on the film, even though the total time of actual exposure was 1 hour and 45 minutes. This does not mean, of course, that no fibering had occurred during the first 1.2 seconds after stretching. It does mean, however, that any possible fibering was extremely small in amount when compared with the results of film 100 (see above). In other words, these x-ray methods showed that a time interval was required to build up the fiber structure. This result was consistent with the longer time required at 380 per cent elongation.

It remained to determine roughly the curve representing the rate at which the fiber structure was built up under these experimental conditions—namely, a cyclic stretch of 420 per cent attained in 0.6 second. This was done by setting the commutator connections (*O* of Figure 1) to open the shutter for approximately 1.5 seconds during each cycle, and by predetermining the time interval between the completion of the cyclic stretching and the opening of the shutter (Figure 2*c*). The total time of actual exposure of all the photographic films was kept at 1 hour and 45 minutes, so that the original negatives could be compared to show the relative intensities of the fiber patterns. Figure 3 is a schematic diagram showing the growth of the fibrous condition in the rubber with the duration of stretch.

There are at least four obvious explanations for the experimental facts of Figure 3. One of these has already been given—namely, that time is required for the transfer of unfavorably oriented molecules out to the boundaries of fibers made up of favorably oriented molecules. It hardly alters the mechanics of this simple picture to assume molecular chains which are twisted like a tangle of twine. Such a modified picture merely substitutes portions of the molecule which is being stretched, for separate molecules which have to be squeezed out of the way. A second possible explanation would be that the time lag is inherent in the process of producing an orientation in those molecules which have become stretched. The first explanation assumes molecules whose ends are aligned in the direction of stretch, but whose middles are pushed out of line so that true orientation requires time. The second explanation assumes molecules whose ends are not aligned in the direction of stretch and assumes that after a time interval the ends, along with the rest of the molecule, succeed in pushing away any conflicting molecules, thus giving a perfect alignment. The authors find this explanation hard to accept because the nearer they are to perfect alignment, the less are the forces tending to produce further alignment of the ends. Because of the length of the molecules, these forces should be much smaller than the forces in the first case. Although the authors do not assign any high degree of probability to the correctness of this second explanation, still it cannot definitely be thrown out. It seems preferable instead to regard it as a variant of the first of the proposed explanations. A third explanation would be that the time lag is inherent in the mechanics of stretching the favorably oriented molecules themselves. So far, such an explanation offers considerable difficulty to the authors, partly because it seems hard to picture the mechanism of a time lag in stretching a simple spiral, and partly because such a picture does not lend itself to the real purpose of a theory; that is, it does not suggest new data and new lines of attack. The fourth explanation is that fibering is delayed merely because of the temporary temperature rise which accompanies the stretching of rubber. The amount of experimental work necessary to confirm or dispose of this explanation is very great, and it will be some time before it can be completed. There are, however, data which make an explanation based on temperature seem highly improbable. Using a thermocouple of fine wire (B. S. No. 30) with a very fine junction imbedded in the rubber strip, it was not found possible to demonstrate experimentally a temperature rise of more than 1° C. even when the rubber was stretched 480 per cent. (This stretch is to be compared with a stretch of 420 per cent in the x-ray experiments.) An equal drop in temperature was measured upon relaxing the rubber strip. Additional evidence against any explanation based on temperature is found in a calculation of the maximum possible rise in temperature due to stretching. A force-elongation curve was plotted for the rubber strip under investigation, using short-time forces. The work of stretching 420 per cent was found graphically. This work was expressed in calories. By the aid of the specific heat of rubber (I. C. T. data) and the mass of the rubber strip, the temperature was calculated which the rubber would have attained if all the mechanical work had been converted into heat and if there had been no heat losses from the surface. This gave a maximum possible temperature rise of 5.2° C. It is hard to believe that such a small temperature rise could seriously reduce the intensity of the diffracted beams of x-rays.

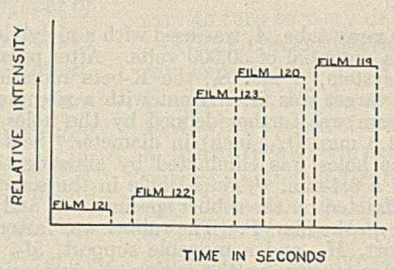

Figure 3. Growth of Fiber Structure

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Alkyl Amines as Solvents

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The determination of the solubilities of over 250 organic compounds in seven of the aliphatic amines at 25° ± 5° C. has permitted the arrangement of these amines, ethyl alcohol, diethyl ether, liquid ammonia, and water in the following order of decreasing solvent ability, where the parentheses include compounds of approximately equal average value as solvents. The order within the parentheses is without significance: (n-butylamine, iso-amylamine, benzylamine, liquid ammonia at −33° C., ethyl alcohol, ethyl ether), (diethylamine, di-n-propylamine ?), (triethylamine, di-n-butylamine), and (tri-n-butylamine, water). The primary amines are thus the best solvents, and the tertiary amines of high molecular weight, the poorest.

The alkyl amines, whose production has hitherto seldom exceeded the scale of the laboratory, have been much less useful commercially than the more readily available aromatic amines, such as aniline. Nevertheless, some attempts have recently been made to prepare the aliphatic amines on a larger scale, and it seems evident that their increased availability will stimulate research to discover new uses to which they may be put. It is hoped that the present paper will be of some value in this connection, since the solubilities of over 250 organic compounds in seven of the aliphatic amines have been determined qualitatively at room temperature (*4*). The data so obtained will allow of a comparison between the solvent properties of the amines and will permit the prediction of solubility relationships in amines with which the authors have not worked.

Experimental Method

It was hoped at the beginning of this work to make fairly accurate determinations of the solubilities of purified organic compounds in all of the lower aliphatic amines, but this proved to be such a task that the greater portion of the solubilities reported were carried out in a semi-quantitative manner at room temperatures (25° ± 5° C.). Accordingly, the experimental method adopted was rather simple.

The organic compounds listed in Table I, after drying in a vacuum desiccator (the liquids were not so dried), were put into individual small stoppered test tubes. These were properly labeled and numbered, weighed to 0.01 gram, and then placed on the laboratory table in front of test-tube racks in which were placed the same number of tubes—empty, stoppered, and correspondingly numbered. (It was advisable to number the stoppers on one set of test tubes to prevent mixing.) Into each of these latter tubes was introduced from a micropipet 0.50 or 1.00 cc. of amine that had been dried over liquid sodium potassium alloy, and redistilled. The tubes containing the amines were always kept tightly stoppered except when solute was being added.

Then a few milligrams of each organic compound were introduced into the correspondingly numbered tube containing the amine. If these first additions dissolved in the course of a few moments (during which time the tubes were gently shaken), further small portions of the organic compounds were introduced, and this process was repeated until the saturation point was reached. This was indicated by the failure of the last portion to dissolve completely. The stoppered tubes containing the organic compounds were reweighed, and these values, subtracted from the weights of the same tubes before the experiment, gave the data from which the solubilities in Table I have been calculated.

Obviously, the method can give results only of a very rough quantitative character. It has therefore been thought best to designate the compounds as slightly soluble, moderately soluble, etc., these designations corresponding approximately to the solubility limits indicated in the table of abbreviations.

The solubility table prepared in this manner contained a number of inconsistencies, and there were also a few results that were obviously in error. A knowledge of the regularities in the solvent power of the amines generally permitted these discrepancies to be picked out at a glance. As an example, it was found that triethyl- and tributylamines were poorer solvents than the corresponding primary or secondary amines. Therefore, if a substance was listed as more soluble in the tertiary amine, the determination was suspected to be in error, and was accordingly repeated. Furthermore, the lower amines were generally distinctly better solvents than the higher amines of corresponding complexity. Thus, a compound was usually definitely more soluble in diethyl- and di-*n*-propylamines than in di-*n*-butylamine, although there were cases where the solubility was not markedly different in the three solvents. *n*-Butyl-, isoamyl-, and benzylamines did not differ very greatly as solvents. With these relationships in mind, it is felt that most of the inconsistencies of the table have been eliminated.

At the conclusion of the solubility experiments, there generally remained a very small amount of undissolved solute. If the amount present was too small, more substance was added and the test tube was warmed, the effect of temperature on the solubility being noted. (This was not done in all cases.) Crystals were often deposited when the warmed solutions were cooled.

A few solubilities in diethylamine were determined quantitatively in the following manner:

A Pyrex tube 20 mm. in diameter and in the form of the letter H constituted the solubility cell. One leg of the H was sealed off at the bottom and closed at the top with a small ground-glass cap. It was through this opening that the dried amine and solute were introduced. In the connecting limb of the H was fused a sintered Pyrex-glass filter plate. The bottom of the other leg of the H terminated in a male ground-glass joint which fitted a corresponding joint on a small graduated receiver (a short length of Pyrex buret, closed at one end). The whole apparatus was rocked for about an hour in a thermostat (at 25.0° C.) with the empty leg above the leg containing the diethylamine. At the end of this time the tube was rotated to allow the saturated solution to flow through the filter into the graduated receiver. The volume of the solution was read, the solvent evaporated off, and the tube weighed. This weight, less the weight of the same tube when empty, gave the amount of substance (or of its reaction product with diethylamine) that had dissolved. From this data was calculated the weight of material contained in 100 cc. of saturated solution, these figures appearing in the diethylamine column of Table I.

The abbreviations used in Table I are as follows:

ABBREVIATION		APPROX. SOL'Y RANGE PER 100 CC. OF SOLVENT *Grams*
ins	Insoluble or extremely slightly soluble	
ss	Slightly soluble	(0^{+} to 10)
s	Moderately soluble	(10^{+} to 40)
vs	Very soluble	(40^{+} to 70)
vs+	More than vs	(70^{+} to 100)
es	Extremely soluble	(100^{+} and above)
misc	Miscible (in methylamine column only)	
∞	Miscible in all proportions	
n	Not soluble to an appreciably greater extent in hot solvent	
x	More soluble in heated amine, crystallizes on cooling	
m	More soluble in heated amine (in some cases because of chemical reaction)	
p	Separates into two liquid phases	
r	Solute reacts chemically with solvent. Reaction is rapid enough to be apparent. All acidic substances react more or less rapidly with amines. (The letter, r, has been omitted in these cases)	
a	Swells	
Numerals	Numerals appearing in diethylamine column indicate number of grams of solute (or of its reaction product with diethylamine) per 100 cc. of solution	

EXPLANATION OF SOLUBILITY TABLE

Since isoamylamine was available in rather limited quantity, solubilities in this liquid were estimated qualitatively, that is, without weighing the amount of added solute.

The solubilities of substances forming highly colored solutions (trinitrotoluene, trinitrobenzene, and most of the dyes) could be estimated only qualitatively because of the difficulty of determining the saturation points.

The solubilities of a few compounds (sugars, polyhydroxyphenols, quinones, and some acids) that appear to undergo a slow reaction with the solvent may not be altogether correct.

For purposes of comparison there have been included the solubilities in methylamine determined by Gibbs (*8*, *6*), the solubilities in ethyl alcohol and in diethyl ether taken from Van Nostrand's Chemical Annual (*2*) and from the Chemiker-Kalendar (*3*), and the solubilities in liquid ammonia at −33° C., as given in Franklin's monograph on nitrogen compounds (*6*).

Blank spaces (where leaders are used) in the table indicate lack of experimental data.

REACTIONS WITH AMINES

Generalities concerning the solubility behavior of classes of organic compounds will be unnecessary, since this information may be obtained with a little effort from Table I. Therefore, the following remarks will be confined to a discussion of some compounds that appear to react chemically with the amines.

ACIDS. Many of the listed acids react immediately with the amines at room temperature, but the reaction is often hindered by the low solubility of the acid (succinic, malic, maleic, and malonic acids). Monochloroacetic acid reacts with the amines with the liberation of heat. Primary and secondary amines appear to attack the chlorine atom of the acid at higher temperatures.

CORK. Cork stoppers are slowly attacked by the vapors of the more readily volatile amines. The vapors of *n*-butylamine appear especially destructive even at room temperatures.

DYES. Solutions of the dyes in the amines are not always the same color as the solid dyes. Thus, crystal violet forms colorless or nearly colorless solutions in all of the primary amines investigated.

ESTERS, ALKYL HALIDES, FATS. The esters, alkyl halides, and liquid fats, in so far as investigated, are miscible with the amines in all proportions, and usually with no apparent immediate reaction. Undoubtedly, reaction would occur in all cases with lapse of time. Benzylamine reacts fairly rapidly with ethyl iodide, ethyl oxalate, and *n*-butyl stearate. The fats appear to be slowly ammonolyzed by the amines, in all probability with the formation of glycerol and a substituted acid amide.

NITRO COMPOUNDS. Nearly all mononitro compounds dissolve in the amines (that is, in the amines investigated in the present work) to form colorless or light yellow solutions. An exception is *p*-nitrophenylhydrazine, which forms a reddish brown solution in *n*-butylamine. 2,4,6-Trinitrotoluene and 1,3,5-trinitrobenzene dissolve in the primary and secondary amines to form deep red or reddish brown solutions. Solutions of a similar color, but less intense, are formed in triethylamine, but the latter may well have contained traces of diethylamine (a possible test for the purity of tertiary amines?). The solutions of these two polynitro compounds in tributylamine were colorless or light yellow.

2,4-Dinitrotoluene dissolves in *n*-butylamine with a blue color which fades to yellow or pale green on heating. The return of the blue color on cooling indicates a reversible reaction whose equilibrium point depends upon the temperature.

The solution of *m*-dinitrobenzene in *n*-butylamine is orange red at room temperatures and yellow at the boiling point of the solvent. The color change is reversible. Picric acid, 3,5-dinitrobenzoic acid, 4,4′-dinitrodiphenyl, and 2,4-dinitrophenol dissolve in the amines to form yellow solutions.

PHENOLS. The polyhydroxyphenols often appear to undergo a slow reaction with the amines in the cold. The increased solubility of some of these compounds on heating may be ascribed in part to chemical reaction with the solvent (salt formation?).

SUGARS. The slow rate of solution of glucose and sucrose in *n*-butyl- and isoamylamines possibly points to a slow chemical reaction between solvent and solute. Thus, fructose is known to react with liquid ammonia (*11*).

Table I. Solubilities of Organic Compounds in Aliphatic Amines

(At 25° ± 5° C.)

		C_2H_5OH	$C_2H_5 \atop C_2H_5$>O	CH_3NH_2	$C_2H_5 \atop C_2H_5$>NH	$(C_2H_5)_3N$	$(n\text{-}C_3H_7)_2NH$	$n\text{-}C_4H_9NH_2$	$(n\text{-}C_4H_9)_2NH$	$(n\text{-}C_4H_9)_3N$	iso-$C_5H_{11}NH_2$	$C_6H_5CH_2NH_2$	NH_3 (−33° C.)
1	Acenaphthene	ssx	..	..	15	sx	..	sx	s	ssx	s	s	ins
2	Acetaldehyde	..	..	misc	..	..	..	..	..	..	..	..	..
3	Acetamide	s	..	vs	ssx	ins	..	s	ins	ins	s	s	vs
4	Acetanilide	vs	ss	..	11	ssx	..	vs	ss	ssx	sx	s	..
5	Acetic acid	..	..	vs	..	..	..	..	..	..	..	..	..
6	Acetoacetic ester	∞	..	..	∞	..	..	..	∞	..	..	..	∞
7	Acetone	∞	∞	∞	..	..	..	..	..	..	..	..	..
8	Acetophenone	∞	..	..	∞	..	..	∞	..	∞	..	..	s
9	*p*-Acetophenylene diamine	..	..	..	ins	..	..	ssx	ssx	..	ssx	..	..
10	*p*-Acetotoluide	ss	s	..	ss	..	..	..	..	ssx	ssx	..	ss
11	Acetylene	s	..	s	..	..	..	..	..	..	..	..	..
12	Acetylene tetrabromide	s	∞	..	r	..	..	..	..	..	..	..	s
13	Acetylsalicylic acid	vs	ss	..	s	s	s	vs	s	ss	vs	s	..
14	Agar-agar	..	..	..	..	..	..	..	..	..	insn	..	ins
15	Alanine	ss	ins	..	..	..	..	..	..	..	insn	..	..
16	Aldol	∞	s	..	∞	..	..	∞	..	..	..	..	..
17	Alizarin	..	..	s	..	..	..	..	..	..	..	..	..
18	Allyl alcohol	∞	∞	..	∞	..	..	..	..	..	..	..	..
19	1-Aminoanthraquinone	ss	ss	..	ss	ss	ss	ssm	ss	ssx	ssm	ss	..
20	*p*-Aminobenzoic acid	s	ss	..	ins	ins	insn	ss	ins	insn	ss	ssx	..
21	*m*-Aminophenol	s	s	..	vs+	ss	..	s	s	ss	vs	s	..
22	*o*-Aminophenol	ss	ss	..	vs	ins	s	vs+	sx	ssn	s	s	vs
23	Aminosulfonic (sulfamic) acid	..	..	..	..	..	..	ssn	..	..	ssx	..	..
24	Ammonium benzoate	..	..	..	ss	..	..	vsr	..	..	vsr	..	vs
25	Ammonium citrate	..	..	..	ss	..	..	..	..	..	..	..	..
26	Amyl alcohol (iso)	∞	∞	..	∞	..	..	∞	..	..	..	∞	..
27	*n*-Amyl formate	∞	∞	∞	..	..	..	..	..	∞	..	..	..
28	Anethole	∞	∞	..	∞	..	..	..	..	..	..	..	ss
29	Anhydroformaldehydeaniline	ss	ss	..	ssn	ssx	ins	ss	ss	ssx	ssx	ssx	..
30	Aniline blue	..	..	..	ss	ins	..	ss	ins	ins	ss	ss	..
31	Anthracene	ss	ss	..	ss	ssx	..	ssx	ss	ssx	ssx	ssx	ins
32	Anthranilic acid	s	s	..	ss	ins	ssx	s	ss	ss	s	s	..
33	Anthraquinone	ss	ss	ss	..	..	..	ssx	..	..	ssx	..	ins
34	Atoxyl	..	..	..	ins	ins	..	ss	ins	ins	ss	ins	..
35	Azobenzene	ss	s	vs	vs	vsx	vs	vs	vs	s	vs	s	s
36	Azoxybenzene	s	s	..	es	..	..	..	..	..	es	..	s
37	Beeswax	..	..	..	s	s	..	s	s	ssm	s	ssm	..
38	Benzalacetophenone	ss	vs	..	vs	..	..	es	..	ssx	..	..	..
39	Benzaldehyde	∞	∞	misc	∞	..	..	..	..	..	..	..	es
40	Benzamide	s	vss	..	ss	ins	s	s	ss	ins	s	s	vs
41	Benzene	∞	∞	..	∞	..	..	∞	∞	∞	..	∞	s
42	Benzidine	s	ss	..	ss	ss	..	s	ssx	ins	sx	s	..
43	Benzil	vs	vs	vs	vs	ss	sx	es	ss	ss	es	es	s
44	Benzoic acid	vs	vs	vs	ssx	ssx	..	vs	s	ssp	s	sx	vs+
45	Benzoic sulfinide (Saccharin)	ss	ins	r	..	..	..	..	..	..	ss	..	..
46	Benzoin	s	..	..	..	..	..	vs	..	..	..	..	..
47	Benzophenone	s	s	vs	es	es	..	es	vs+	sx	es	es	s
48	Benzyl acetate	∞	∞	..	∞	..	..	..	∞	..	..	∞	s
49	Benzyl alcohol	∞	∞	..	∞	..	..	..	..	∞	..	..	∞
50	Borneol	vs	vs	..	es	..	..	..	..	..	..	..	s
51	*o*-Bromoacetanilide	..	..	vs	..	..	..	..	..	..	..	..	..
52	*p*-Bromoaniline	vs	vs	..	esx	vs+	esx	vs+	vs	ssx	vs	vs+	..
53	Bromcamphor	s	vs	..	vs+x	s	..	vs+x	vs+	ssx	vs	vs	..
54	Bromocresol green	..	..	..	ss	ins	..	s	ssn	ins	s	s	..
55	1-Bromonaphthalene	∞	∞	..	∞	..	..	..	..	∞	..	..	..
56	*p*-Bromonitrobenzene	s	s	..	s	..	..	..	..	..	..	..	..
57	*o*-Bromotoluene	s	..	..	∞	..	..	..	∞	∞	..	∞	..
58	*p*-Bromotoluene	s	s	..	es	..	..	..	es	..	..	..	..
59	*n*-Butyl alcohol	∞	..	..	∞	..	..	..	..	..	∞	∞	∞
60	*tert*-Butyl alcohol	..	..	∞	..	..	..	..	..	..	..	..	..
61	*n*-Butyl cyanide	∞	s	..	∞	..	..	∞	..	..	∞	..	s
62	*n*-Butyl ether	∞	∞	..	∞	..	..	∞	∞	∞	∞	..	..
63	*n*-Butyl formate	∞	∞	..	∞	..	..	..	∞	..	..	..	..
64	*n*-Butyl stearate	..	..	..	∞	..	..	∞	∞	∞	∞	rss	..
65	Caffeine	ss	ss	..	ss	..	..	ssx	..	..	ssx	..	ss
66	Calcium acetate	ins	..	..	insn	..	..	..	..	..	..	..	..
67	*n*-Calcium butyrate	..	..	..	..	..	..	insn	..	..	..	..	..
68	Calcium formate	ins	..	..	..	..	..	..	..	..	insn	..	..
69	*d*-Camphor	es	vs	..	es	es	..	es	vs	vsx	es	es	vs
70	Carbon disulfide	∞	∞	..	r	..	..	esr	..	∞	..	..	r
71	Casein	..	..	..	ins	ins	..	ins	ins	ins	ins	ins	..
72	Cellulose	ins	ins	..	ins	ins	..	ins	ins	ins	ins	insa	ins
73	Cellulose acetate	..	..	..	ss	ins	ins	es	ins	ins	s	s	es
74	Cellulose nitrate	..	..	..	s	ins	..	vs	ss	ins	vs	vs	s
75	Cerulein	..	..	vs	..	..	..	..	..	..	..	..	..
76	Cetyl alcohol	s	s	vsx	..	..	..	es	..	s	..	..	ins
77	Chloroacetic acid (mono)	s	s	..	srx	vsxp	..	sx	ssxr	ssp	vs	ssrm	vs
78	*p*-Chlorodiphenyl	s	s	..	vs+	vs+x	..	vs	vs	sx	vs	vs	..
79	Chloroform	∞	∞	∞r	∞	..	..	..	..	..	..	..	sr
80	Cholesterol	ssx	s	..	..	..	vs+	..	..	..	vs+	..	ins
81	Chromotropic salt	..	..	..	..	..	..	insn	..	..	..	..	..
82	Cinchonine	ss	ss	..	..	..	..	ssn	..	..	ssx	..	ins
83	Cinnamic acid	s	vs	..	s	ss	..	sx	ss	ssx	s	ssx	s
84	Coconut oil	..	..	..	∞	∞	..	∞	∞	∞	∞	∞	..
85	Copal	..	..	..	..	..	..	..	..	..	insn	..	ss
86	Crystal violet	..	..	..	ins	ins	..	vs	ins	ins	s	s	s
87	Cyclohexanol	s	s	..	∞	..	..	..	..	..	..	..	..
88	*o*-Dianisidine (bianisidine)	s	vs	..	ss	ins	..	sx	ss	ins	s	s	..
89	Diazoaminobenzene	s	vs	..	vs	..	..	..	..	..	es	..	vs
90	*p*-Dibromobenzene	s	..	..	40	vs+x	..	vsx	vs	sx	vs	vs+	ss
91	2,3-Dibromopropyl alcohol	vs	∞	..	∞	..	..	..	..	..	..	..	..
92	Dichloramine-T	..	..	..	vsr	sr	..	vsr	ssr	r	vsr	vs+r	r
93	*p*-Dichlorobenzene	es	vs	..	53	esx	..	es	ves	vs+x	esx	es	ss
94	Dichlorogallein	..	..	s	..	..	..	..	..	..	..	..	s
95	Dichlorohydrin	∞	∞	..	∞	..	..	..	..	..	..	..	..

Table I. Solubilities of Organic Compounds in Aliphatic Amines (*Continued*)

(At 25° ± 5° C.)

		C_2H_5OH	$\begin{matrix}C_2H_5\\C_2H_5\end{matrix} > O$	CH_3NH_2	$\begin{matrix}C_2H_5\\C_2H_5\end{matrix} > NH$	$(C_2H_5)_3N$	$(n\text{-}C_3H_7)_2NH$	$n\text{-}C_4H_9NH_2$	$(n\text{-}C_4H_9)_2NH$	$(n\text{-}C_4H_9)_3N$	iso-$C_5H_{11}NH_2$	$C_6H_5CH_2NH_2$	NH_3 (−33° C.)
96	2,3-Dihydroxyquinoxaline	..	..	..	..	..	..	insn	..	..	..	..	s
97	Dimethylaminoazobenzene	x	..	..	sx	ssx	ssx	sx	s	ss	s	s	..
98	*p*-Dimethylaminobenzaldehyde	s	s	..	..	..	..	sx	..	..	..	..	..
99	Dimethylaniline	s	∞	..	∞	..	..	..	..	..	..	..	ss
100	Dimethylethylcarbinol	s	s	..	∞	..	..	..	∞	..	∞	∞	..
101	Dimethylglyoxime	vs	vs	..	ssx	s	ssx	vs	ss	ssx	vs	s	..
102	2,6-Dimethylquinoline	vs	vs	..	vs	..	..	..	..	..	..	..	..
103	2,2-Dinaphthylamine	ss	..	..	ssx	ssx	ssx	sx	ssx	ssx	s	ss	..
104	2,4-Dinitroaniline	ss	..	vs	..	..	..	..	..	..	..	..	..
105	*m*-Dinitrobenzene	ssx	..	vs	9.3	ss	..	s	ss	ssx	s	s	..
106	3,5-Dinitrobenzoic acid	vs	ss	..	ss	ss	ssx	s	ss	ssx	vs	sm	..
107	4,4′-Dinitrodiphenyl	ss	vs	..	ss	ss	..	ssx	ssx	ssx	ssx	ssx	..
108	2,4-Dinitro-1-naphthol-7-sulfonic acid	..	..	..	ss	..	..	..	..	..	..	..	..
109	2,4-Dinitrophenol	ss	vs	..	ss	..	..	sx	..	ssn	vs	..	vs
110	2,4-Dinitrotoluene	ss	..	vs	sx	..	..	sx	ssx	ssx	..	..	ss
111	Diphenyl	ss	s	..	41	s	..	vs	s	sx	vs	vs	ss
112	Diphenylamine	vs	vs	..	es	vs	es	es	vs	sx	es	es	..
113	Diphenylbenzamide	..	..	..	ss	..	..	..	..	..	ssx	..	..
114	Diphenylguanidine	..	..	..	ss	ins	..	vs	s	ssx	vs	s	..
115	Diphenyl ketoxime	..	..	vs	..	..	..	..	..	..	..	..	..
116	Diphenyl sulfone (phenyl sulfone)	ss	s	..	ssx	ssx	..	ssx	ss	ssx	ssx	sx	..
117	Diphenylurea (sym.)	s	s	..	ss	ins	..	ss	ss	ssx	s	ssx	s
118	4,4′-Dipyridyl (bipyridine)	vs	..	..	..	..	..	vsx	..	..	sx	..	vs
119	Di-*p*-tolylselenide	..	..	..	..	..	..	es	..	..	..	..	..
120	Eosin	s	..	..	ss	ins	..	vs	ss	ins	vs	s	s
121	Ethyl alcohol	∞	∞	..	..	..	..	..	∞	..	..	∞	..
122	Ethyl carbonate	s	..	..	ssr	..	..	∞	..	..	..	∞	sr
123	Ethyl cyanoacetate	∞	∞	..	∞	..	..	..	..	..	..	..	..
124	Ethylene dibromide	s	∞	spr	∞	..	..	..	∞	..	..	∞	..
125	Ethylene glycol	∞	ss	..	∞	..	∞	..	..	..	∞	..	..
126	Ethyl iodide	s	s	..	∞	..	..	..	..	∞	..	esr	s
127	Ethyl malonate	∞	∞	..	∞	..	..	..	∞	..	∞	..	..
128	Ethyl oxalate	s	..	..	∞	..	..	..	∞	..	..	ssr	..
129	Ethyl sulfate	..	..	..	r	..	..	..	rs	..	..	..	..
130	Fluorene	ss	vs	..	13	ssx	sx	s	s	ssx	s	s	ins
131	Fluorescein	vs	ss	..	ss	ins	..	s	ins	ins	s	s	s
132	Galactose	ss	..	vs	..	..	..	..	..	..	..	..	..
133	Gallein	..	..	ss	..	..	..	..	..	..	..	..	..
134	Gallic acid	s	ss	..	insn	insn	..	s	insx	insn	s	ssm	s
135	Gelatin	..	..	..	ins	ins	..	insn	ins	ins	ins	ins	..
136	Glucose	ss	ins	vs	ss	ins	ssn	vs+	ins	ins	s	s	vs
137	β-Glucose pentaacetate	ss	ss	..	..	..	..	es	..	..	..	..	..
138	Glycerol	∞	ins	vs	..	..	..	..	..	..	..	..	..
139	Guaiacol	∞	∞	..	∞	..	..	..	..	..	..	..	..
140	Guanidine nitrate	..	..	..	ss	..	..	..	..	..	..	..	vs
141	Gum arabic	..	..	..	insn	ins	..	ins	ins	ins	ssn	ss?	..
142	H acid	ss	ss	..	..	..	..	insn	..	..	..	..	..
143	Hemoglobin	..	..	..	ins	..	..	insn	..	..	..	..	ss
144	Hexaethylbenzene	s	vs	..	..	..	..	ssx	..	..	ssx	..	..
145	Hexamethylenetetramine	ss	ins	..	ssn	..	..	ssn	..	..	..	..	..
146	Hippuric acid	ss	vss	vs	ssx	..	..	..	..	..	vs	..	vs
147	Hydrazine sulfate	ins	..	..	ins	..	..	..	..	..	..	..	insr
148	Hydroquinone	vs	vs	vs	35	ss	s	s	s	ss	s	ssx	vs
149	Hydroxylamine hydrochloride	s	ins	vs	..	..	..	..	..	..	..	..	..
150	Indigotin	ins	ins	vs	ins	ins	..	ss	ss	ss	ins	ss	ss
151	Indole	vs	vs	..	es	..	..	es	..	..	..	..	vs
152	Isatin	s	ss	..	..	..	..	vs	..	..	..	..	s
153	Isoquinoline	∞	∞	..	∞	..	..	..	∞	..	∞	..	s
154	Lactose	ss	ins	..	ss	ss	..	ss	ins	ins	ss	ins	vs
155	Lanolin	..	..	..	es	es	..	es	es	es	es	es	..
156	Linseed oil, raw	..	..	..	∞	∞	..	∞	∞	∞	∞	∞	..
157	Lysol	..	..	..	∞	..	..	..	..	..	..	..	..
158	Maleic acid	s	ss	..	ins	ins	..	ssn	ins	ins	ssx	insm	
159	Malic acid	vs	ss	..	ins	ins	ins	ssn	ins	ins	ssn	ssx	ss
160	Malonic acid	s	ss	..	ins	insn	insx	ss	ins	ss?	ss	ins	ins
161	Mannite	ss	ins	..	ss	ins	..	ss	ins	ins	ssn	ins	ss
162	*d*-Menthol	vs	vs	..	es	es	es	es	es	es	es	es	es
163	Mercuric acetate	ss	..	..	insr	ins	s	vs	ss	ins	ss	ins	s
164	Mercuric cyanide	s	..	vs	..	..	..	es	..	ssn	..	..	vs
165	Mercury diphenyl	ss	..	..	ss	ins	ss	ss	ss	ins	ss	ins	..
166	Mercury di-*p*-tolyl	..	..	..	..	..	..	ssx	..	ssx	ssx	..	..
167	Methanol	∞	∞	∞	..	..	..	∞	..	∞	..	..	..
168	*meso*-Methyl acridine	vs	vs	..	..	..	..	..	..	..	es	..	..
169	Methylene aminoacetonitrile	..	..	..	ss	ss	..	ss	ins	ssx	ss	ins	..
170	Methylene dianiline	..	..	..	insn	ss	..	ss	ss	insx	ss	ss	..
171	Methyl orange	ss	ins	ss	ins	ins	ins	ssn	ins	ins	ss	ss	..
172	Mucic acid	ins	..	..	ins	ins	insn	ss	ins	ins	ss	ins	s
173	Naphthalene	ss	vs	..	27	sx	..	vsx	s	sx	vs	sx	ss
174	Naphthionic acid	ss	ins	..	ss	ins	..	s	ins	ins	s	ss	..
175	1-Naphthol	vs	vs	vs	..	..	..	..	..	..	..	..	..
176	2-Naphthol	vs	vs	vs	es	vs+	..	es	es	vs	es	es	ss
177	Naphthol yellow	..	..	..	ins	ins	..	ss	ins	ins	ins	ins	..
178	Night blue	..	..	..	s	s	..	s	s	s	s	s	..
179	*p*-Nitroacetanilide	s	ss	..	ss	..	..	..	..	..	..	..	..
180	*m*-Nitroaniline	s	ss	..	sx	ssx	..	s	ss	ssx	s	s	s
181	*p*-Nitroaniline red	..	..	..	ss	ss	..	s	ssx	ssx	s	s	..
182	*m*-Nitrobenzaldehyde	vs	vs	vs	..	..	..	..	..	..	..	..	..
183	Nitrobenzene	∞	∞	∞	..	..	..	∞	..	∞	..	..	vs
184	*m*-Nitrobenzenesulfonamide	..	..	vs	..	..	..	..	..	..	..	..	..
185	*o*-Nitrobenzoic acid	s	s	vs	..	..	..	..	..	..	..	..	..
186	*p*-Nitrobenzoic Acid	ss	ss	..	ssx	insn	ssx	vsx	ss	ss	s	sx	ss
187	*p*-Nitrobromobenzene	ss	..	..	ss	ss	ssx	sx	ss	ssx	s	sx	..
188	*o*-Nitrophenol	vs	vs	vs	..	..	..	..	..	..	..	..	..
189	*p*-Nitrophenol	vs	s	..	13	ss	ssx	vs	ss	ssm	vs	s	s
190	*p*-Nitrophenylhydrazine	..	..	..	..	..	..	vs	..	ssx	..	..	..

Table I. Solubilities of Organic Compounds in Aliphatic Amines (*Concluded*)

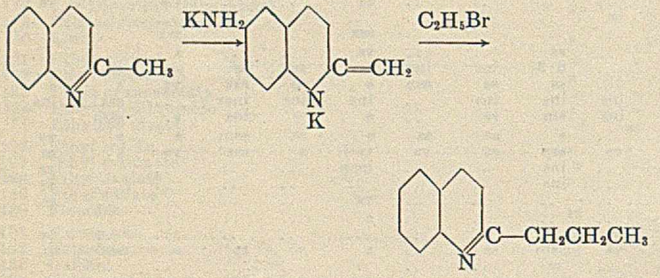
(At 25° ± 5° C.)

		C_2H_5OH	$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}>O$	CH_3NH_2	$\begin{matrix}C_2H_5\\C_2H_5\end{matrix}>NH$	$(C_2H_5)_3N$	$(n\text{-}C_3H_7)_2NH$	$n\text{-}C_4H_9NH_2$	$(n\text{-}C_4H_9)_2NH$	$(n\text{-}C_4H_9)_3N$	$\text{iso-}C_5H_{11}NH_2$	$C_6H_5CH_2NH_2$	NH_3 (−33° C.)
191	*o*-Nitrotoluene	∞	∞	vs	..	..	..	..	..	..	..	..	..
192	*p*-Nitrotoluene	s	s	..	vs+x	..	..	..	..	sx	vsx	..	..
193	3-Nitro-4-toluidine	vs	..	...	sx	..	..	vsx	..	ssx	..	..	s
194	Nitrourea	vs	vs	..	ins	..	..	..	..	..	..	..	vs
195	Oleic acid	∞	∞	..	∞	∞	..	∞	∞	∞	∞	∞	ins
196	Olive oil	..	..	..	∞	∞	..	∞	∞	∞	∞	∞	..
197	Orange IV	..	..	..	ss	ins	..	ss	ss	ins	ssn	ss	..
198	Oxalic acid.2H₂O	s	ss	..	ins	ins	..	insn	insn	ins	ins	ins	ins
199	Oxanilide	ss	ss	..	0.5	..	..	..	..	..	..	..	..
200	Palmitic acid	ss	..	vs	..	..	..	..	..	..	..	..	..
201	Paraffin	..	..	..	ss	sx	..	s	sm	sx	s	ssx	ins
202	Paraffin oil	..	..	..	∞	..	..	∞	..	∞	..	..	..
203	*n*-Pentane	∞	..	∞	..	..	..	..	..	..	..	..	..
204	2-Pentene	..	..	..	∞	..	..	..	..	..	..	..	..
205	Penacetin	ss	ss	..	ss	ins	ssx	s	ss	ssx	s	ss	..
206	Phenanthrene	ss	s	..	s	..	..	..	..	..	..	vs	ins
207	Phenol	∞	∞	vs	es	..	..	..	..	..	es	..	vs
208	Phenolphthalein	s	ss	vs	s	ss	..	s	ss	ss	s	s	..
209	Phenylacetic acid	es	vs	vs	..	..	..	vsx	..	..	..	..	..
210	*meso*-Phenyl acridine	ss	s	..	..	..	..	..	..	..	ssx	..	..
211	Phenylazo-1-naphthylamine	..	..	..	..	..	..	..	..	ssx	s	..	..
212	*o*-Phenylenediamine	vs	vs	..	..	..	..	sx	..	..	sx	..	vs
213	Phenylglucosazone	ss	..	..	..	..	..	sx	..	..	vs	..	vs
214	Phenylhydrazine	∞	∞	∞	..	..	..	..	..	..	..	..	..
215	Phenylmercuric bromide	..	..	..	..	..	..	ssx	..	..	ssx	..	..
216	2-Phenylquinoline	vs	vs	..	vs	..	..	vs	..	..	s	..	..
217	Phenyl-*p*-tolyl sulfone	..	..	..	6.3	ins	ins	ss	ss	ssx	ssx	ss	..
218	Phenyl urea	vs	vs	..	ss	ss	ssn	s	ss	ssx	vs	s	s
219	Phthalic acid	s	ss	ins	ins	ins	..	ins	ins	insx	..	ssx	ins
220	Phthalic anhydride	s	ss	ins	sm	ss	..	s	ss	ins	s	ssm	..
221	Phthalimide	s	ss	..	s	ss	ss	s	sx	ssm	s	s	vs
222	Picric acid	s	ss	vs	ssp	ss	vs	vs+	s	ssx	vs	s	es
223	Potassium amide	r	ins	..	ins	..	..	insn	..	..	..	..	vs
224	Potassium ethyl sulfate	..	..	..	ins	..	..	..	..	..	..	..	vs
225	Potassium quinaldine	r	vs	..	..	..	..	vs	..	..	..	..	es
226	Potassium triphenylmethyl	r	s	..	..	..	..	s	..	..	..	..	..
227	Pyridine	∞	∞	∞	..	..	..	..	..	..	..	..	∞
228	Pyrogallol	vs+	vs+	vs	ssm	ss	..	s	s	ss	s	sm	es
229	Pyrrole	vs	vs	..	∞	..	..	..	..	..	..	..	..
230	Quinaldine	vs	vs	..	∞	..	..	∞	..	∞	∞	..	s
231	Quinaldine picrate	ss	..	..	es	..	..	es	vsx	ss	..	..	..
232	Quinine	es	vs+	..	s	ssm	s	vs	ssm	ss	vs	s	insol
233	Quinoline	s	..	..	∞	..	..	∞	∞	∞	..	∞	∞
234	Quinoline methiodide	..	..	..	..	..	..	vsx	..	..	vs	..	vs
235	Quinoline yellow (water soluble)	..	..	..	ins	ins	..	ss	ss	ins	ssn	ss	..
236	Quinone	vs	vs	sr	vsr	..	..	..	..	..	..	..	..
237	Resorcinol	es	vs	vs	s	..	..	vs	..	..	..	..	es
238	Rosaniline	s	ins	vs	ins	ins	..	ss	ins	ins	ss	ss	s
239	Rosin	vs	vs	..	s	s	..	vs	vs	ins	s	s	insr
240	Rosolic acid	ss	s	..	ss	ss	..	s	ss	ss	s	s	ss
241	Rubber, vulcanized	ins	ins	..	a	a	..	a	a	a	a	ins	ins
242	Salicylic acid	vs	vs	..	vs	sp	sx	vs+	ss	ssm	es	s	..
243	Selenium	ins	ins	..	ins	ins	..	ins	ins	ins	ins	ins	ins
244	Shellac, white	..	..	..	ins	ins	..	ins	ins	ins	insn	ins	..
245	Skatole	s	..	..	es	..	..	..	..	es	..	..	s
246	Soap	..	..	..	..	..	..	ins	..	..	ins	..	ins
247	Sodium alizarin sulfonate	..	..	..	ss	ins	..	s	ss	ins	s	s	ins
248	Sodium benzoate	ss	..	..	insn	..	..	insn	..	..	..	..	..
249	Sodium indigo sulfonate	..	..	..	ins	ins	..	ss	ins	ins	ss	ss	..
250	Sodium-*p*-nitrophenylantidiazotate	..	..	..	..	..	..	vs	..	..	..	..	s
251	Starch (corn)	ins	ins	..	ins	ins	..	ins	ins	ins	ins	ins	insa
252	Stearic acid, tech.	ss	s	..	es	vs+	es	es	vs+	vs	vs	ssx	ins
253	Strychnine	ins	ins	..	..	..	..	ss	..	..	..	..	..
254	Succinic acid	s	ss	ins	insn	ss	ssx	ins	ins	ins	ins	ssx	..
255	Succinimide	s	..	..	ss	ins	s	vsx	ss	ssx	sx	ss	..
256	Sucrose	ss	..	vs	ss	ss	..	vs	ins	ins	s	vs	vs
257	Sulfanilic acid	ss	ss	..	ssn	ss	..	s	ss	ss	s	ss	vs
258	Sulfonal	ss	ss	..	..	..	..	ssx	..	..	ssx	..	s
259	Sulfur, rhombic	ins	ins	..	s	s	..	vs	ss	ssx	s	s	s
260	Tallow	..	..	..	vsx	..	..	..	..	..	es	..	..
261	Tannic acid	ss	ss	..	ss	ins	insn	ss	ins	ins	ss	ss	ss
262	Tartaric acid	s	ss	ins	ins	ins	..	ss	ss	insn	ss	ssx	ins
263	Tetraethylammonium iodide	..	..	..	ins	ins	..	ins	ins	insn	ins	ins	ss
264	Tetraethyl lead	∞	∞	..	∞	...	..	∞	..	..	..	..	..
265	Tetrahydronaphthalene	vs	vs	..	∞	..	..	∞	..	∞	..	..	..
266	Tetramethyldiaminobenzophenone	vs	vs	..	0.6	ss	ssx	ss	ss	ssx	ssx	ssx	ss
267	Tetraphenyl lead	..	..	..	..	..	..	ssx	..	..	ssx	..	..
268	Tetraphenylmethane	..	..	..	ss	ss	ss	ssx	ssx	ssx	ssx	ssx	ss
269	Thymol	vs	vs	vs	es	es	es	es	es	vs	es	es	vs
270	*o*-Tolidine	vs	..	..	s	ss	ssx	s	ss	ssx	s	s	vs
271	Toluene	∞	∞	∞	..	..	..	..	..	∞	..	..	..
272	*p*-Toluenesulfonamide	..	..	..	vs	ss	vs	vs+	s	ssx	vs	s	s
273	*p*-Toluidine	s	s	..	es	vs+	..	es	vs+	sx	es	es	vs
274	Trichlorogallein	..	..	ss	..	..	..	..	..	..	..	..	..
275	2,4,6-Trinitroaniline	ins	..	es	..	..	..	..	..	..	..	..	..
276	1,3,5-Trinitrobenzene	ss	vs	..	es	ss	sp	s	ss	ss	s	s	vs
277	2,4,6-Trinitrotoluene	ss	vs	..	s	ss	sp	vs	ss	ss	s	s	s
278	Triphenylmethane	ss	vs	..	25	s	sx	s	s	ss	s	s	..
279	Triphenylselenonium iodide	..	..	..	..	..	..	ssn	..	..	ssn	..	..
280	Tyrosine	ins	ins	..	ss	ins	ins	ss	ins	ins	ss	ins	..
281	Urea	ss	ss	vs	ins	ins	..	ss	ins	ins	ss	ss	s
282	Uric acid	ins	ins	ins	..	..	..	..	..	insn	insn	..	ins
283	Wax, carnauba	..	..	..	ss	..	..	..	..	..	..	..	..
284	Wax, Japan	..	..	..	vs	..	..	..	..	..	..	..	..
285	*m*-Xylene	vs	vs	∞	..	..	..	..	..	..	..	..	..
286	1,3,5-Xylenol	s	..	..	es	vs+	..	es	vs	vs	es	es	..
287	Xylose (crude)	ins	ins	..	es	..	..	s+	..	..	s	..	..
288	Zinc stearate	..	..	..	ss	ins	ss	vs?	ss	ins	s?	s	..

Sulfur. Sulfur is crystallized, apparently unchanged, from hot solutions of the tertiary amines. Primary and secondary amines at first dissolve sulfur, then react chemically with it, possibly in the manner that sulfur reacts with liquid ammonia (*10*). Here a portion of the sulfur appears to be reduced to ammonium sulfide or polysulfide, while a corresponding amount is nitridized ("oxidized") to sulfur nitride, N_4S_4.

Reactions in the Alkylamines

The numerous researches of Franklin, Kraus, and their co-workers (*6*, *7*) have demonstrated the scientific value of liquid ammonia as a solvent in which chemical reactions may be carried out. With the expectation of finding in the alkylamines higher-boiling solvents in which many of the same reactions could be effected, it was shown that 2-*n*-propylquinoline was synthesized in *n*-butylamine almost as readily as in liquid ammonia (*1*). The reaction is expressed by the following equations:



In the first stage of the reaction, solid potassium amide is dissolved by a *n*-butylamine solution of quinaldine to form potassium quinaldine, which is rapidly converted to 2-*n*-propylquinoline (and potassium bromide) by the action of ethyl bromide. It is therefore possible to utilize the alkylamines as solvents for chemical reactions.

Comparison of Solvent Power of Amines, Ethyl Alcohol, Diethyl Ether, and Ammonia

In view of the relatively small number of compounds listed in Table I, and because of the qualitative nature of the solubility determinations, it is not possible to make an accurate intercomparison of the solvent power of the amines, alcohol, ether, ammonia, and water. This is additionally true because of the many gaps in the table which were not filled because it was thought that the missing solubilities could be predicted from the observed regularities in the solvent ability of the amines. Nevertheless, a rough idea of the relative value of these liquids as solvents may be gained in the following manner: The compounds listed in Table I have been divided into two classes—substances of definite solubility (s, vs, vs+, es) and substances of low solubility (ss, ins). The comparison is then made between the percentages of the compounds examined that are of definite solubility. (Liquids and mixtures, such as paraffin and lanolin, have been excluded in this comparison.)

The liquids of Table II may be arranged in the following approximate order of decreasing solvent power: (*n*-butylamine, isoamylamine, benzylamine, ammonia at −33° C., ethyl alcohol, diethyl ether), (diethylamine, di-*n*-propylamine?), (triethylamine, di-*n*-butylamine), (tri-*n*-butylamine, water). The order of arrangement within the parentheses is without significance.

The conclusion may therefore be drawn that the primary amines are the best solvents, and that the amines of lower molecular weight are usually better solvents than the higher amines of the same type. Diethyl- and di-*n*-propylamines would appear to be of about equal solvent ability, judging from the limited number of experiments with the latter solvent.

The substitution products of water (ethyl alcohol and diethyl ether) are about equally good as solvents for the compounds examined, while the substitution products of ammonia (primary, secondary, and tertiary amines containing the same alkyl radicals) differ considerably among themselves. Franklin (*5*) and Hurd (*9*) have made comparisons of the chemical properties of these substitution products of water and of ammonia.

Methylamine probably will prove to be superior to the other amines as a solvent when more experimental data are available. Liquid ammonia at room temperatures should prove a slightly better solvent than either *n*-butyl- or isoamylamine.

Acknowledgment

The three butyl amines used in this work were provided by the Commercial Solvents Corporation, to whom the authors wish to express their indebtedness.

Nearly all of the chemical individuals listed in Table I were high-grade preparations of the Eastman Kodak Co., Kahlbaum, or the Gesellschaft für Teerverwertung (Duisberg-Meiderich). The di- and triethylamines were obtained from the Eastman Kodak Co., and the isoamyl- and diisopropylamines from Kahlbaum. The benzylamine was prepared in this laboratory by Mr. Liang.

Table II. Comparative Solvent Power

Solvent	H_2O	C_2H_5OH	$(C_2H_5)_2O$	NH_3	$(C_2H_5)_2NH$	$(C_2H_5)_3N$
ins, ss	144	68	57	46	100	96
s, vs, vs+, es	22	86	69	67	66	30
Total solubilities	166	154	126	113	166	126
Total determinations that are s, vs, vs+, es, %	13	56	55	59	40	24

Solvent	$(C_3H_7)_2NH$	$C_4H_9NH_2$	$(C_4H_9)_2NH$	$(C_4H_9)_3N$	$C_5H_{11}NH_2$	$C_6H_5CH_2NH_2$
ins, ss	29	64	90	115	64	57
s, vs, vs+, es	22	108	38	21	97	71
Total solubilities	51	172	128	136	161	128
Total determinations that are s, vs, vs+, es, %	43	63	30	15	60	56

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New Resins of the Phenolphthalein Series

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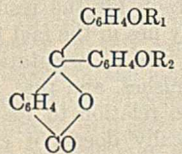
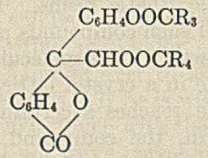
The problem of this research was to find new resins from phthalic anhydride and from phenol. As the first object for research, phenolphthalein was chosen, since it is the simplest and most accessible condensation product of those two substances. Up to the present, it has been known that phenolphthalein, when heated above its melting point (250° to 280° C.), yields a dark brown resin, soluble in alkalies, with a red coloration characteristic of the sodium salt of phenolphthalein. This solubility may be explained in two ways: either the conversion into a resin does not proceed fully; or the resin hydrolyzes under the influence of alkalies with the formation of the initial product. Because of its property of becoming colored under the influence of alkalies, its insufficient chemical resistance, and the dark color of its film, phenolphthalein, fused as a resin, has found no practical application. Kienle (*3*) tried to condense phenolphthalein with glycerol and formaldehyde; the product with glycerol is half liquid and cannot be regarded as a resin. The condensation product with formaldehyde (although like Bakelite in its properties) has no technical and, more important, no economic advantage over Bakelite.

Study of Phenolphthalein Esters and Ethers

The structure of phenolphthalein ethers and esters is as follows:





These derivatives have very unusual properties; the esters, with the exception of a few which will be referred to later, show all the properties of the so-called pseudoresins, described by Eibner (*1*) and others. In a freshly fused condition, they are resin-like, transparent, lightly colored substances, which after a certain length of time become partly or wholly crystalline and therefore strongly resemble the natural resin, elemi, or the esters of abietic acid.

While not going into the possible theoretical explanation of the conversion of resins into the crystalline state, it is necessary only to mention that the rate of conversion for different esters is different. It is, for instance, very slow for phenolphthalein benzoate, being evidenced only by a slight turbidity of the resin surface a few months after its preparation; and it is very rapid for phenolphthalein acetate or butyrate. Complete turbidity of the whole mass occurs a few days after its preparation.

In general it was possible to establish that the rate of conversion is in direct ratio to the molecular weight of the ether or ester radical, and is more rapid for esters than for ethers. In order to check this regularity, a series of esters and ethers were prepared: phenolphthalein acetate, butyrate, benzoate, phthalate, salicylate, benzene sulfate, toluene sulfate, stearate, palmitate, methylate, ethylate, benzylate, toluylate, glycolate, etc.

The methods employed were the usual ones for obtaining phenol esters. Phenolphthalein methylate and ethylate were obtained by the action on phenolphthalein, in alkaline solution, of an excess of dimethyl and diethylsulfate, the mixture being vigorously shaken; phenolphthalein acetate was obtained by boiling phenolphthalein with acetic anhydride; the butyrate, benzoate, phthalate, salicylate, benzene sulfate, toluene sulfate, stearate, and palmitate, by heating the dry phenolphthalein sodium salt with an excess of the corresponding arylchloride. The purification of the esters was achieved by first passing steam through the products of the reaction, then shaking the product with dilute alkali (1 per cent solution), with water, and finally drying at a temperature near 100° C.

From the above-mentioned series of ethers and esters, the phenolphthalein toluylates are noteworthy because of their exceptional properties, including complete stability. While phenolphthalein benzoate (nearest the toluylate in chemical character) is a substance with two clearly expressed forms—one being resin-like after fusion, and the other crystalline after recrystallization—the phenolphthalein toluylates are real resins, and to modify them or to isolate a crystalline part by the usual methods was found to be impossible. Phenolphthalein benzylate after fusion remains a long time without change, but if it is dissolved in hot acetone or benzene, and then cooled, white crystals are precipitated, which may be collected and purified. If a dense solution of phenolphthalein benzylate (resin) is made in acetone, benzene, or benzene with alcohol, etc., with or without a plasticizer or oil, this solution, when poured into a glass or on a metal surface, forms a lacquer film which in a short time becomes turbid, owing to crystallization. Phenolphthalein toluylate behaves quite differently. Lacquer films of the latter resin made with alcohol-benzene, drying oil, etc., do not become turbid and remain transparent and brilliant.

Physical Properties of Phenolphthalein Toluylates

Phenolphthalein toluylate from *m*-toluyl chloride melts, according to the method of Ubbelode, at 67–83° C. (depending upon the degree of purification); that from *o*-toluyl chloride melts at 70–85° C. The saponification value of the *m*-toluylate, after boiling 1 hour with an alcohol solution of potassium hydroxide, is 70–88; its acid value is about 2. Toluylates, after evaporation of the solvent, form almost colorless films; these are brilliant, solid, waterproof and, still more important, have exceptional resistance to solutions of alkalies and acids. Thus it may be rightly said that the non-crystallizing ethers of phenolphthalein represent a new and, at the same time, a very fine type of synthetic resin. The authors gave this resin the name of "alkalite," because of its high resistance to alkalies. Its industrial value is evident if alkalite is compared, in respect to its resistance to alkalies, with already-known natural and synthetic resins, paraffins, asphalts, etc.

In Table I are shown the results of tests on various materials. The resistance to alkalies was determined by soaking a piece of the sample, having a measured surface, in a 10 per cent solution of caustic soda (5 cc. of alkali per square centimeter of surface) with a subsequent titration of the alkali with a 0.1 *N* solution of potassium permanganate after a definite length of time. If before the first titration the sample went to pieces, the titration was not effected. The quantity of potassium permanganate per square centimeter was taken as the measure of solubility of the sample in alkali. This method with potassium permanganate has been tested and

TABLE I. RESISTANCE OF DIFFERENT MATERIALS TO ALKALIES

MATERIAL	TIME *Days*	$KMnO_4$ *Cc.*	TIME *Days*	$KMnO_4$ *Cc.*	TIME *Days*	$KMnO_4$ *Cc.*	TIME *Days*	$KMnO_4$ *Cc.*
Ceresin, commercial (80%)	7	2.75	16	1.92	26	4.35	55	4.89
Ozocerite from Cheleken (70–72%)	7	2.64	16	2.12	26	5.14	55	5.74
Ozocerite from Fergana	7	1.99	16	2.21	26	4.46	55	4.98
Ozocerite from Dagage	7	2.41	16	1.50	26	3.32	55	4.20
Paraffin	7	2.64	16	2.64	26	4.09	55	3.84
Asphalt from Syria	7	3.40	16	1.46	26	3.64	55	4.43
Gilsonite	7	1.19	15	6.17	32	2.76	58	4.43
Carbolite F[a]	7	Complete destruction						
Carbolite G[b]	7	6.16	16	13.05	26	14.12	55	14.95
Bakelite No. 251[c] (extra hard)	7	Complete destruction						
Idytol[d]	10	Complete destruction						
Glyptal (stage C)	7	Complete destruction						
Leikorite[e]	7	Complete destruction						
Pertinax[f]	10	23.36	20	27.84	45	26.72	..	..
Phenolacrolein resin	10	25.67	20	29.64	45	33.62	..	..
Congo copal (agero)	7	1.61	15	5.22	32	4.85	58	7.88
Congo copal (warlée)	7	3.61	15	Went to pieces				
Dammar	7	Went to pieces						
Kauri	7	Went to pieces						
Phenolphthalein toluylate 1	7	1.57	15	5.01	32	3.36	58	4.10
Phenolphthalein toluylate 2	7	2.90	16	2.90	26	5.01	55	5.67
Phenolphthalein benzylate	7	0.53	15	4.57	32	3.01	58	5.24

[a] Phenol-formaldehyde resin formed in presence of sulfonic acids produced from petroleum acid sludge.
[b] Cresol-formaldehyde resin formed in presence of fatty and sulfonic acids produced from petroleum acid sludge.
[c] Phenol-formaldehyde resin as made by Bayer Co.
[d] Phenol-formaldehyde resin formed in presence of hydrochloric acid.
[e] Phenol-formaldehyde resin formed in presence of milk acid.
[f] Laminated material prepared from sheet paper impregnated with solution of phenol-formaldehyde resin.

has proved reliable in the laboratory of the Section for the Study of Materials at the All-Union Electrotechnical Institute in Moscow. Details of this method are given in the work of Florensky and Andrianow (*2*).

As may be seen in Table I, the majority of the materials were destroyed by alkalies even before the first titration, i. e., before 7 days had passed. Ceresin, ozocerite, paraffin, asphalt, Congo copal ("agero"), and the phenolphthalein toluylates gave the best results. Therefore, in resistance to alkalies, phenolphthalein ethers may compete with the natural resin, copal. The authors hope to be able to prepare other non-crystallizing phenolphthalein ethers and to perform similar tests on them in the near future.

CHEMICAL CONSTITUTION OF PHENOLPHTHALEIN ETHERS

The first analysis of phenolphthalein benzylate (melting point 153.5° C.) showed 80.23 per cent carbon and 5.54 per cent hydrogen; if the formula were $C_{34}H_{26}O_4$, the analysis would be 81.93 per cent carbon and 5.22 per cent hydrogen; and if the formula were $C_{34}H_{28}O_5$, the analysis would be 79.07 per cent carbon and 5.43 per cent hydrogen. The first analysis of meta-phenolphthalein toluylate (melting point 67° C.) showed 80.34 per cent carbon and 5.69 per cent hydrogen; if the formula were $C_{36}H_{32}O_4$, the analysis would be 82.13 per cent carbon and 5.70 per cent hydrogen; and if the formula were $C_{36}H_{34}O_5$, the analysis would be 79.41 per cent carbon and 5.51 per cent hydrogen. Therefore, by their composition these ethers are a mixture of phenolphthalein derivatives with a closed and an opened anhydride chain.

They are monomers, as is seen from their molecular weight determined by the cryoscopic method in benzene:

	Mol. Wt.		*Mol. Wt.*
Benzylate 1	490	Toluylate 1	500
Benzylate 2	472	Toluylate 2	543
Av.	481	Av.	521
$C_{34}H_{26}O_4$	498.2	$C_{36}H_{32}O$	528.2
$C_{34}H_{28}O_5$	516	$C_{36}H_{34}O_5$	546.2

Therefore, phenolphthalein toluylate should be classified as a resin-monomer; monomers are seldom to be found among synthetic resins. The reason for the resinous condition of such compounds probably lies in the fact that, with the growth of the molecule, the rate of orientation of the molecule in a crystal lattice diminishes, and that, when the molecule reaches a certain size in relation to its structure and form, the compound practically does not crystallize. In the series of phenolphthalein ethers, beginning probably with phenolphthalein toluylate, the absence of the crystallization capacity is noted, and it is very likely that higher phenolphthalein esters will give resins still more perfect.

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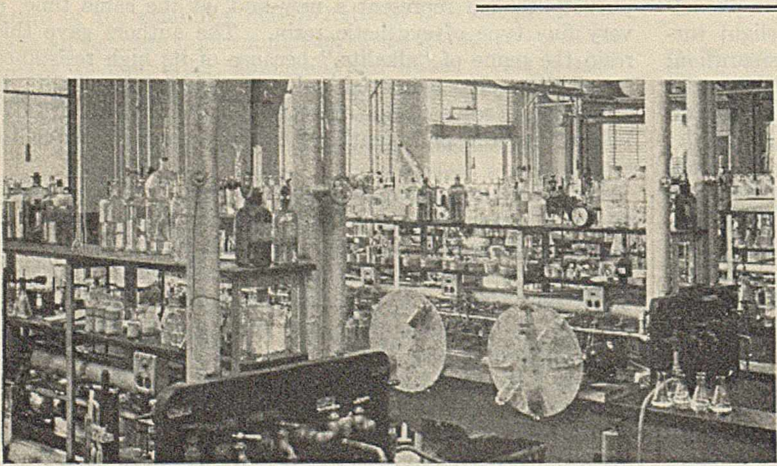


View of Organic Chemistry Laboratory, Eastman Kodak Company

Management of Research

Commencing a Series of Articles to Consider the Functions of Laboratory Organization and the Coördination of Laboratory and Plant Effort.

Scope of Research Management

C. E. K. Mees, *Director of Research and Development, Eastman Kodak Company, Rochester, N. Y.*

THE function of management in relation to industrial research may be divided into three sections:

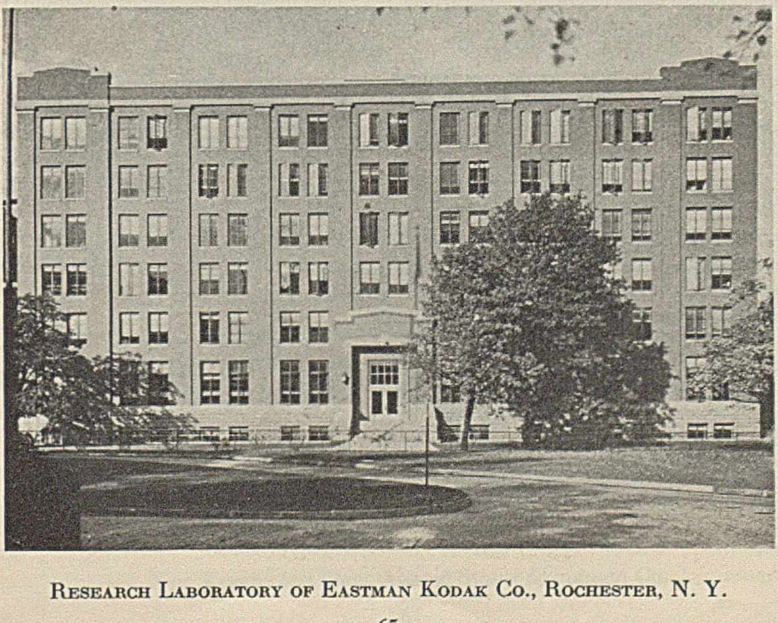
(1) The provision of the necessary staff, equipment, and supplies.
(2) A decision as to what investigations are to be undertaken and the allotment of problems to the staff.
(3) The utilization of the results obtained.

C. E. K. Mees

Selection of Research Staff and Equipment

The selection of the research personnel and the provision of the necessary equipment unquestionably comes within the scope of management. In a small laboratory the director himself will select his entire staff, will handle the personnel problems as they arise, and with the aid of perhaps one assistant will control the purchase of supplies and the provision of facilities. In a large laboratory it will be necessary for him to delegate much of this work, selecting personally only the senior members of the staff and handing over to assistants all the purchasing and control problems. If he is wise, however, the director will certainly keep in touch with the greater part of the research staff and will not leave personnel problems too much to other people. The art of management is primarily the art of managing men.

In the management of a research laboratory it is very desirable to avoid over-organization and red tape. The men working in such laboratories are of a very independent and critical type of mind and are extremely impatient of bureaucratic methods. It is undoubtedly a great mistake to allow research work to be directed by administrators who have no real sympathy with the results of the work and who attempt continually to standardize and regulate things which, in themselves, are incapable of standardization and regulation. It is an advantage for the scientific worker to have the administrative burdens of the laboratory arranged for him so that when he wants apparatus or assistance, or when he wants materials prepared, or lantern slides made, he can get them by simple request. Order and regularity are also an advantage. Regular hours of work are really better than irregular hours in the long run, and there is no disadvantage in having a proper system of conducting conferences, discussion, etc. But too much administration is as bad as too little, and there is a good deal of danger that the office, which should be the servant of the investigator, may become the master.

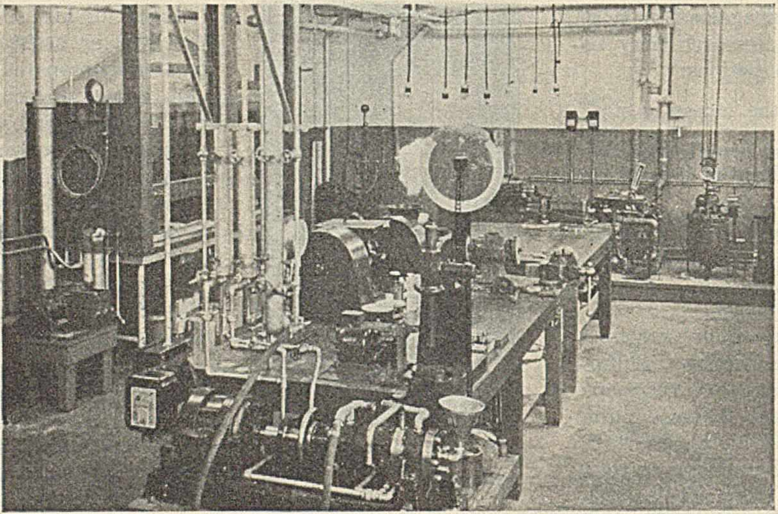


Research Laboratory of Eastman Kodak Co., Rochester, N. Y.

Selection and Allotment of Investigations

In discussing the scope of management in relation to the direction of the research itself, the main consideration must be the effect of any plan of management upon the results produced. This may seem quite obvious, but in management of all kinds it is not uncommon to find that the plan tends to be regarded as an *end* in itself rather than as a *means* to an end, and in research the end, and the only end, is *results*. The only justification for the work of an industrial research laboratory is its production of new and improved products, methods, and processes, and the management which produces the largest amount of new products, methods, and processes at the lowest cost is *ipso facto* the best management.

Since the production of results in research is a purely psychological process, it follows that the management of research will depend upon the psychology of the research worker. Research workers are of many different types, and an elastic outlook on the part of the management is a dominant factor in the production of the best results. However efficiently a laboratory may be organized and however energetically the staff may endeavor to produce results, if they do not have the inspiration to make the discoveries which should follow applied research effort, the laboratory will be sterile. Results in research cannot be obtained by hard work alone; moreover, elaborate planning, which is such an important factor in modern production, can easily be a disadvantage in research. The situation is perhaps analogous to that of war. To go to war without a plan is quite fatal. To go to war with a rigid plan which cannot be changed as fresh circumstances arise may also be fatal. One of the great disadvantages of the immense complexity of modern mobilization for war is that, once mobilization has commenced, it must be carried through on the lines laid down regardless of changes which may arise in the conditions, since to make any change is impossible until the operation is complete. Rigidity of plan must be avoided at all costs in the organization of industrial research. The management must not only be able to adapt its methods to the psychology of the workers, but it must also be able to change its plan of research as the work develops and as discoveries are made. This mobility involves a management in exceedingly close touch with the practical research worker, so that his psychology may be understood and so that the plan of work may be modified as events develop.



Laboratory for Technological Chemistry, Eastman Kodak Co.

And we thus come to the ideal organization of research, which may be stated in a few words: "getting good research men and letting them do what they want to." In practice this limit of disorganization cannot be achieved in an institution of any size. All the research men will not be equally good. All of them cannot direct their own work, and a laboratory in which all the workers were free to do whatever they wanted would probably end in confusion, marked by a considerable amount of individual disagreement. We must therefore introduce some form of departmental organization, so that the different fields of work are to some extent delimited. The actual planning of the research work may then be entrusted to the department head, who is necessarily a thoroughly qualified investigator in close touch with the men under his control.

One of the great problems of the research director will be the desire of the management for definite plans, preferably accompanied by accurate estimates of the cost of the work, their conception being that research can be charged ahead with the same precision as construction or production. This is not true, but the director may have to make concessions to the management and produce such plans and estimates. Both he and the management are fortunate if that is not the case. A general plan of research is valuable; a detailed plan has in all probability much less value. A general estimate of cost may be of use; a detailed estimate is merely an invitation to the laboratory accounting department to fake its figures when they do not agree with the estimate. It is perfectly reasonable that the management should desire to know what each piece of work will cost in order that it may consider whether the work shall be started, but in practice such estimates have very little value because the rate at which the work will be done cannot be foreseen except in the vaguest way. The financial administration of the research laboratory really amounts to no more than allocating a certain amount of money to research, and leaving it to the research director and his staff to spend that money to the best advantage. If a piece of work for which men have been engaged and for which funds have been allocated proves promising, it is generally desirable to transfer more men to it and to spend more money. If it seems to get less promising as the work is done, it is usually better to diminish the expenditures and transfer the men to other fields. The general rule for research is the same as that for any other form of gambling—"Cut your losses, and let your profits run." Research is essentially a speculation, but it differs from most speculations in that the odds seem to be weighted heavily in favor of the speculator, so that if industrial research is undertaken with competent men and is allowed to carry on in the face of difficulty and failure, profit is almost inevitable.

Utilization of Results

When a piece of work has been completed, the utilization of the results will often offer a serious problem for the management of the laboratory. The methods by which the management of a laboratory can ensure the most efficient use of the results obtained will depend very much upon the organization of the industry itself, and the whole subject of the application of research will no doubt be dealt with later in the series.

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Logical Divisions of a Research Organization

Francis C. Frary, *Aluminum Company of America, New Kensington, Pa.*

IT IS impossible to lay down any hard and fast scheme of dividing or grouping the personnel of a research organization which would be generally applicable. The types of problems to be solved, the size of the organization, its scope, and relation to other technical units in the same company, and especially the training and ability of the men available, determine the divisions which it is logical to make. The whole problem is one of best utilizing the available man power for the purpose in hand.

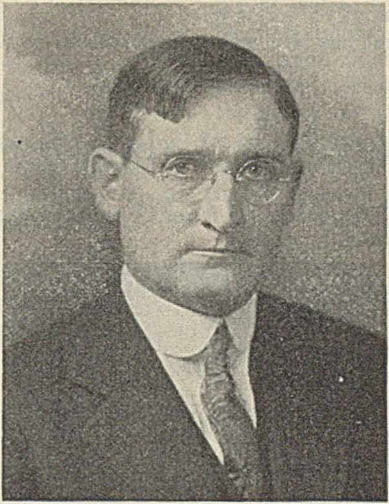

Photo by Bachrach

Francis C. Frary

In general, if the organization is large enough, certain service divisions, as distinguished from research divisions, arise naturally. Thus, the accounting division and the library, including filing and abstract service, are naturally differentiated from the rest of the organization at an early stage of development. In some cases, a separate division for repairs, maintenance, and construction develops naturally, while in others such functions will be taken care of by the plant organization to which the research unit is attached.

As the organization grows, it is probably wise in most cases to develop an analytical laboratory as a separate service division, manned and staffed by specialists, and prepared to do most of the necessary analytical work more economically and satisfactorily than the individual research men could do it for themselves. This group will include in its functions the development and simplification of suitable rapid and reliable analytical methods for the control of the quality of the company's products and raw materials, as well as for process control. It will also supervise and check the plant laboratories, if the company is large enough to have several of them, and represents the company in questions where analytical results are involved.

Similarly, if there is much physical testing, a separate division of specialists for this work may become desirable. Its general functions resemble, in its field, those of the analytical group. They include research on testing methods and on the physical properties of the company's products and raw materials.

Rolling "Strip-Roll" Aluminum Sheet

New Kensington Plant, United States Aluminum Co.

Other engineering functions may also be assigned to this group, unless there are so many that it seems desirable to separate the engineering from the testing work.

In some cases, separate sections for botany or geology, or for either physics or physical chemistry, may be desirable. There will, of course, be one or more chemical research divisions, depending on the type and variety of the chemical problems studied. The old grouping of organic and inorganic may suffice in some cases; in others, special groups will have to be constituted to handle certain types of problems, such as electric furnace research, rubber, paint, textiles, paper products, dyes, pharmacology, etc. A separate division for semiplant-scale development may be advisable in some cases; a group for such work must, in any event, be provided in one or more places in the organization, if manufacturing processes are to be studied and improved.

Metallurgical research, when included in the program, will be separated from the chemical work, if in sufficient volume to justify it. Metallographic service work, alloy development, metal-working processes, etc., may be included here. In smaller organizations, it is customary to include the physical testing of metallurgical products in this group, although in larger organizations a separate testing division has advantages.

Patent work, if carried out in the research unit, requires a separate and highly specialized group. If this work is handled by outsiders, one or more members of the research organization should be assigned the duty of coöperating with the patent attorneys or patent department, and acting as "contact men." They represent the patent group in the technical staff to see that patentable inventions are not lost, and that the attorneys get proper technical advice and assistance. Most inventors and research men have rather vague notions of patent matters, and considerable study and pains are required to insure that the company is properly protected in its enjoyment of the results of its research and development work.

In this analysis I have assumed that the research department is attached to a manufacturing company, or similar organization, and that its problems are basically chemical and mechanical, in the broad sense of these terms. If the unit is independent, or in the consulting field, or primarily interested in medicine or some other line, much of what has been said may not fit the case. On the whole, however, we may say that the divisions of a research organization must be determined on a common-sense basis by its management, taking into consideration its size, type, and scope, and that the extent of subdivision will have to be decided by the circumstances in each case.

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Principles of Research Laboratory Management

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G. W. Thompson

Before taking up a discussion of this subject as expressed in the title, there are certain fundamental principles with reference to industrial research organizations which first should be discussed, and there are certain assumptions to be stated. To justify the formulation of any principles of management in a research laboratory, we must assume that the laboratory is an established affair or, at least, is accepted as becoming an established affair. There is no need to discuss principles of management in a research laboratory that is organized for one or a few specific objectives; nor is it worth while to discuss principles of management unless they can be applied on a long-time basis. Furthermore, there can be no principles of management really worth stating unless the laboratory is a fairly large one and employs such a number of men that some subdivision of work and real organization are required. There is one other very broad essential—namely, that a research laboratory be recognized as an important part of the business organization by which it is supported.

A research laboratory searches for knowledge, particularly in its own field. Two things are important in this connection: one is an insatiable thirst for knowledge; the other is ample library and record facilities where this knowledge can be sought, orderly assembled, and stored away. There are continuous demands made upon the research laboratory for information in regard to the products manufactured and their uses. Purely commercial men can hardly be expected to have this knowledge in accurate form, and they must rely upon the research laboratory to give it to them in that form and to correct from time to time the erroneous opinions which are apt to be developed where lack of accurate knowledge exists. A thorough search and orderly assembly of available knowledge is also a necessary requirement in all research projects.

It cannot be expected, of course, that every member of a research laboratory will have, to the same high degree, a thirst for knowledge, but this should be the mainspring back of the workers in a good research laboratory. A thirst for knowledge is essential, as otherwise there will not be built up that power of anticipating answers to inquiries which often come, as it were, from a clear sky. A thirst for knowledge, resulting in its acquisition and assembly, will always tend towards keeping a research laboratory ahead of the game. It will be seen from this that it should be made up largely of men who are students, who like study, and who are not afraid to put many weary hours, extending through months and sometimes years, on problems confronting them. This is the distinction between a commercial laboratory and a research laboratory. The pressure of commercial demands upon the former do not permit much time to be given to research study. Quick results must be obtained from them. In a research laboratory, while there must be a certain willingness to be driven and to report promptly knowledge already acquired, there must also be an unwillingness to be driven unduly on problems requiring study and careful investigation.

An industrial research laboratory is presumed to exist to satisfy commercial needs. It must contribute something to industry, and especially to the particular industry supporting it, to justify its existence. There is this distinction, therefore, between an industrial research laboratory and those laboratories engaged in pure research. The latter may contribute to industrial needs, but that is not their main purpose. An industrial research laboratory must contribute to the commercial needs of the industry. Undoubtedly, in many industrial research laboratories true pure scientific research is carried on. It is, however, usually limited to the field of the industry. Otherwise it is questionable whether it can be justified. This close relation existing between the commercial needs of an industry and its research laboratory may at times present difficulties. What the selling or producing parts of an industry may demand of a research laboratory are possibly unreasonable both as to substance and form. The question may be raised as to whether expenditures for research are justified unless results are obtained which are of immediate commercial advantage. Sometimes, although fortunately less now than in days gone by, demands have been made on the research laboratory by those in charge of commercial problems for reports in forms that result in obscuring the truth. Naturally, the research laboratory cannot conform to such demands, for it is essential in research work that there be a devotion to truth as it is seen. The old question as to what constitutes truth is unsolved as much here as elsewhere. In view of these difficulties we must presume that the research laboratory has confirmed itself, in the minds of those in control of commercial operations, as being an important part of the organization, and that it is depended upon for help, truthful information, and an earnest endeavor to supply the organization's needs, patiently, arduously, and devotedly.

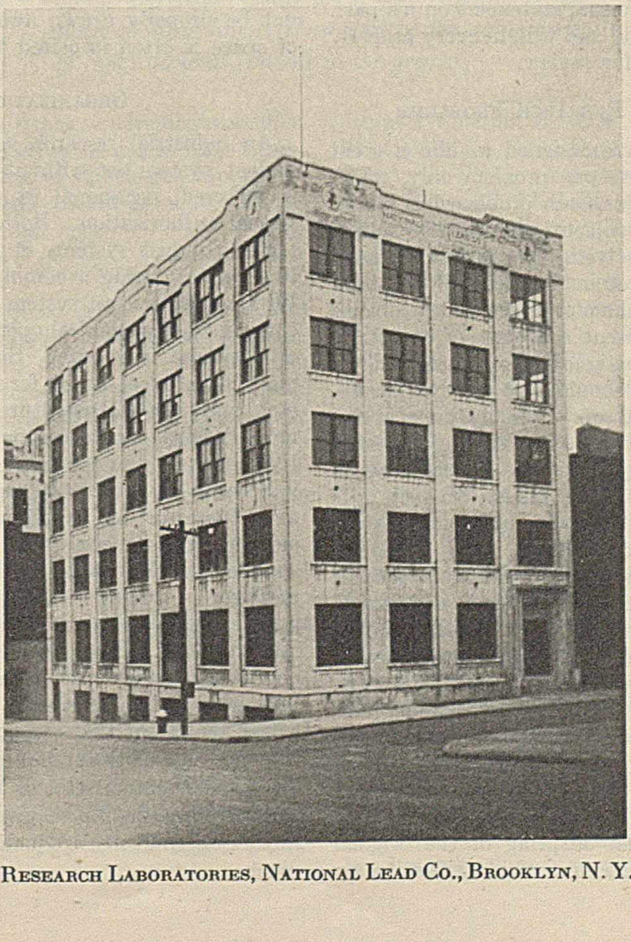
With this picture (not by any means ideal) of the kind of research laboratory of which the principles of management are to be discussed, we come now to the real subject of the paper. It will be treated under several heads:

Personnel organization.
Organization of records.
Organization with reference to field covered.
Methods of handling research problems.
Laboratory planning.
Organization of finances.

Personnel Organization

Every research laboratory, of the kind which is being discussed, finds it necessary to employ a large number of persons having nothing to do directly with research. These are the ones engaged in clerical and mechanical work. If the scope of the work planned is extensive, it may be necessary to employ men for the designing of machinery and apparatus, and even for the building of such machines in their initial form. The main and important work of the laboratory, however, is done by chemists, physicists, and engineers. Each of these is selected with a presumption of ability for certain particular lines of work. Very often, however, it is found necessary to try a new employee on different kinds of work before determining that for which he is most suited. Occasionally it is found that a man, presumed by the information available to be the best suited for a certain class of work, turns out after a time to be unable to solve the problem confronting him. In such a case the man must be transferred to other work, and someone else put on the problem; or else his services are no longer required. Usually such a man will relieve the management of responsibility and find other work himself because of the discouragement he has suffered. Such a case is no direct reflection upon the individual; it illustrates the point that not all of us are equally equipped to do the same kind of work. Sometimes the trouble with such a man is due to the fact that his education has told him more of what he cannot do rather than having suggested to him ways and means whereby things can be done. Parenthetically, that knowledge which tells persons what cannot be done is the most injurious form of learning.

The head of a research laboratory cannot be expected to know the personal abilities and limitations of all of his associates. He has to work through heads of departments and take their opinions. At the same time he ought to be continually cognizant of the success or failure of the various workers in the organization. There should be that *esprit de corps* between the members of the organization which results in proper recognition of good workers, without overlooking delinquencies.



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Organization of Records

Of the utmost importance is the proper preservation of records and their proper filing and indexing. These records begin with every sample as it comes to the laboratory or arrives in the course of research work, whether it be for analytical work or work that does not depend upon prior analysis. These samples should be carefully identified as to their origin, date, right number, from whom received, and the purpose for which received. The samples themselves differ as to the length of time they should be kept. Some should be held permanently. I am referring of course to the surplus left after examination. There is nothing more exasperating in the research laboratory than to find that samples have been thrown away on which valuable work has been done, and to which reference is found in the records. Attempts have been made by certain methods of marking to insure the saving of such samples, but beyond this it is difficult to go, and, in spite of such a system, important samples are often lost. Sometimes the trouble comes from imperfect marking or improperly attached labels.

The same is true in handling the records. It is hard to distinguish between the papers that should be kept and those which, after a certain period of time, can be discarded. There must be distinction made, however, as otherwise what is kept may become so voluminous as to make it difficult to find what is wanted. While the library is not necessarily a part of the recording system, it is important that the librarian be substantially in charge of the recording system. Very often he is requested to make a library study of a certain subject that leads to a study of the records. In other words, records are depositories of knowledge. They come, therefore, in the same category as the library.

The form in which records are kept depends largely upon their scope. Preferably all of the papers on a certain subject should be bound together in one or more flexible binders so as to be kept together and not be subject to scattering. My own preference is for the letter size sheet which can be filed unfolded. The old foolscap size is usually an annoyance.

Since the library is included as a part of the records, the following remarks may be appropriate here. The library should be a study wherein anyone in a laboratory can read. The members of the force should be permitted to take books to their desks, cards being left in the library as to where they are; and with some restrictions they should even be permitted to take these books home if desired. The library should cover everything relating to the field of the industry that can be obtained. There should be a sufficient number of general books on every branch of chemistry and physics. Al journals relating to the industry, with few exceptions, should be available. Some of these should be bound at the end of the year and the others should be stored, at least for a period of time. Trade journals of course ought not to be kept more than a short time.

Organization with Reference to Field Covered

Obviously, if the field is large enough, it must be subdivided into several divisions, and the work under each head still further subdivided. The director of a laboratory cannot be expected to have as much knowledge in each of the fields comprised by the industry as those heads under him should possess. He may have some form of knowledge based, perhaps upon long experience, which is invaluable when passing upon the work and recommendations of heads under him. He must have a knowledge sufficient, in reference to each of these heads, to enable him to give some guidance to the work they are doing or projecting and to be at all times ready to discuss their problems with them. Sometimes it may be desirable for the head of the laboratory to have men working directly under him doing work of which he sees the importance and which, because of his personal interest, he wishes to handle directly. This is perfectly proper, providing the men working for him come to him frequently and fully understand his objectives. Sometimes it will be found, however, that employees so engaged might work far better under the direction of a lower head. The question of how many heads should exist under the manager depends upon the laboratory and the capacity of the heads under him. It may be better to have only two or three heads and let them subdivide the work. There is no hard and fast rule relating to subdivision. It ought not, however, to be carried so far as to destroy the unity of the whole. Certain policies must be determined by the manager of the laboratory or must have been determined through long association with the work without formal statement on his part. Variations of these policies should and will, in every properly organized laboratory, come in for review.

Methods of Handling Research Problems

Sometimes one man may have assigned to him a great many problems, or he may have one problem only, which may be large or small. Every research problem has its objective, and very often, if the objective is properly stated, the problem is more than half solved. There may be, however, a series of objectives evolved in the course of the study of the main objective. We therefore see that problems subdivide themselves and represent a process of evolution. First a project is laid out and assigned to one man, with or without assistants. His study should first involve a careful review of the literature and work already done in the laboratory. Then work is started. After a certain amount has been finished, a preliminary report is presented which indicates the next step or steps to be taken. In fact, it is quite usual that a number of separate consecutive steps are found to be involved. Each of these is an outgrowth of the original project. It is doubtful whether, in the development of the study of a research problem, any logical order prevails. If logic does prevail, it is probably noted after the fact. The important thing, however, whether logical or not, is the proper laying out of research projects. Each one should be carried to such a point that it would indicate some other research project, unless indeed, as is unusual, the matter is completely and satisfactorily solved. Let me emphasize the thought that is here outlined: every research problem passes through a state of evolution, and each step becomes an individual offspring of the original project and deserves a certain amount of identification by a separate report. What its progeny may be should also be indicated.

Laboratory Planning

The laboratory is the housing and may be the home of research operations. It must be laid out with regard to the field covered by the research. Just how elaborately it shall be built and equipped depends upon the money available and the purpose which those authorizing the expenditure of money may have in mind. All of us are familiar with the imperfect and inexpensive equipment used by the early chemists. We do not want a research laboratory to be dependent upon such facilities, and yet the question may properly arise as to how far research laboratory expenditures should go in providing expensive edifice and expensive equipment. I really have no opinions on this subject; "handsome is as handsome does," and I am sure that all real research workers are better pleased by proper room and facilities than they are by fanciful decorations. The building should house a suitable library. It should provide general office space and telephone connection between departments. It should have a room for the receiving of supplies and preparation of samples; and refuse should be delivered daily to this room. The question of subdivision is a debatable one. Much space is often lost by such subdivision. Those rooms assigned for certain men to work in may be unavailable for other use. For this reason, although I may be wrong, I have resisted the idea of subdivision. A certain number of private offices are necessary. One of these private offices, perhaps, can be used for relatively large gatherings, if desirable. But to divide the main floors where research is being done, into separate rooms simply for the purpose of segregating the workers and their work does not appeal to me. Certain subdivisions must be made where offensive gases or vapors are given off, and where such cannot be properly drawn away, but beyond this the utility of space is often impaired by walls and corridors.

Organization of Finances

An industrial research laboratory may work under the budget system or without it. No matter which system is followed, occasional expenditures must be covered by special authorization. Both systems have their disadvantages. Budget systems imply previous knowledge of work to be done during a coming year which is hard to foresee. Without the budget system there is an implication of confidence in the economical operation of the laboratory. Whatever system is adopted, there should be a careful record made of the expenditures for salaries, supplies, rent, insurance, etc., and these expenditures should be classified with as much detail as can be reasonably expected. By this classification one is able to compare expenses from year to year, and, if increases are noticeable, a check can be made to see whether such increases are justifiable. A complicated system of accounting is unnecessary. The purchase of apparatus and supplies should not be made without the approval of the manager or others in authority, when expenditures exceed a certain stated amount for any one item or group of closely related items. Economy must be exercised. The man in charge of purchases must be continually on the alert to determine whether apparatus ordered cannot be supplied by a transfer rather than by purchase.

Where a given research problem has been studied arduously for a sufficient length of time without practical results, consideration should be given in conference as to whether further expenditures are justified, for how long, and for how much.

CONCLUSION

A research laboratory is an organization made up of human beings with all the advantages and limitations which that involves. In my opinion, the more really human are the members of a research organization, the more successful it will be. Or, to put it another way, the less it operates along the lines of discipline, such as we think of in connection with the army, the more successful it will be. The enthusiasm of a worker must never be dampened, although properly it may be directed. He should always be encouraged when he shows a thirst for knowledge. All that may be necessary is tactfully to guide his thirst for knowledge to the particular problems on which he should be working.

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Flow of Petroleum Lubricating Greases—I

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PETROLEUM lubricating greases[1] *are dispensed and used as lubricants under a variety of conditions in which the factors determining the flow characteristics are of primary importance. Based on a novel principle, a viscometer which predetermines the rate of shear, and which is especially designed for the purpose of measuring the flow characteristics of lubricants, is described.*

The data at 77° F. (25° C.) on several worked cup greases and a pulp oil are presented in graphical form. The large range of rate of shear reported (0.08 to 132,000 reciprocal seconds) covers the complete practical range of use. Among others, the following conclusion is drawn: The apparent viscosity of greases decreases with increasing rates of shear in a manner characteristic of the particular soap used, approaching in the limit a value higher than, but of the same order of magnitude as, the oil in the grease.

IT HAS long been recognized that the actual lubrication of rubbing surfaces must be accomplished by a fluid film if satisfactory results are to be obtained. Not so generally recognized is the fact that, when greases are employed, the lubrication must be accomplished by a fluid film, rather than by the soap structure itself. As a rule, greases are used as a matter of convenience in handling and application, rather than for any peculiar lubricating properties. Many mechanisms are constructed so that oil lubrication would be either impractical or extravagant. For this reason the lubricant used must possess those characteristics which permit it to be held in containers which are not liquid-tight, and to feed to the surfaces only when actual motion occurs. The consistency requirements of different mechanisms are almost as varied as the mechanisms themselves. In the past no basic data of sufficient completeness have been available which would permit accurate estimation of the needs of any particular case.

IMPORTANCE OF RATE OF SHEAR

The viscosity of a lubricating oil is its most important property, being fixed if the temperature and total pressure are fixed. (Variation with total pressure is very small in the normal range.) The analogous property of a grease, termed the "apparent viscosity," is not fixed under the above conditions but varies with the rate of shear. Table I shows the rate of shear in a simplified case of a film between a 2-inch (5-cm.) journal and concentric with its bearing when the speed and clearances are as specified.

TABLE I. RATE OF SHEAR IN CONCENTRIC BEARING

(Speed, 1800 r. p. m.)

CLEARANCE		RATE OF SHEAR
Inch	*(cm.)*	*Seconds*$^{-1}$
0.01	(0.025)	18,800
0.001	(0.0025)	188,000
0.0001	(0.00025)	1,880,000

In the simple case of a material flowing through a tube of $^1/_8$-inch (0.32-cm.) bore at a rate of 3 cc. per second (0.4 pound per minute), the rate of shear is approximately 1000 seconds^{-1}. It appears then that an extremely large range of rate of shear is involved in the use of lubricants. In dispensing and in feeding from cups and boxes the rate of shear involved is usually in the comparatively low range from 0–1000 seconds^{-1} and in the lubricating film from 1000 seconds^{-1} to indefinitely large values.

The foregoing shows the importance of providing an instrument capable of producing various rates of shear over a very large range. The numerous control instruments, though very useful in their fields, are not suitable for this research because of their restriction to a narrow range of rate of shear, usually very low in magnitude. In most cases it is impossible, in the absence of other data, to translate the data from such instruments to absolute units because of the complex function of rates of shear involved. Particularly illustrative are the Saybolt tube, with its variable head, and the A. S. T. M. cone penetrometer, with its double-taper cone. The MacMichael and Stormer instruments come a little nearer to being applicable to the problem but are only suitable for use on thin greases, and cover only a comparatively narrow range in rate of shear.

The use of applied pressure on liquids and plastics in capillary-tube viscometers to effect various rates of flow is well known (*2*, *6*). Pressure-viscosity data have been obtained on a variety of compositions, including paints, lacquers, emulsions, and gels of many kinds (*1*, *2*, *6*). It is the common experience of workers in this field that, when these methods are applied to lubricating greases, certain difficulties are frequently encountered. Grease lumps and air pockets alter the rate of flow, and blow holes occur in the charge. These occurrences are evident only from the fact that the data do not check a previously determined value. Bulkley and Bitner (*5*) managed to circumvent the difficulty of irregular flow by attaching a perfectly horizontal calibrated capillary through a trap to the metering capillary and noting the rate of movement of a mercury plug therein. Their instrument has the further advantage that the same sample can be used repeatedly.

CONSTANT-SHEAR VISCOMETER

To avoid the above difficulties and to effect greater precision and ease of operation, a method, believed to be novel, has been developed, consisting simply in fixing the rate of

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[1] The term grease is used throughout in the restricted sense of a soap-thickened mineral lubricating oil.

flow (with a given capillary, therefore the rate of shear) and measuring the resultant pressure at the entrance to the capillary. This principle is illustrated diagrammatically in Figure 1.

When a piston, *P*, is driven mechanically at a constant rate into a cylinder, *C*, the sample, *S*, is forced downward against the mercury bed, *Hg*, and out through capillary *O* mounted in the removable support, *D*. Mercury is displaced through a duct to the gage until equilibrium is reached, at which time all the flow is through the capillary. The rate of efflux (or the rate of flow in centimeters per second) is thus predetermined by the speed of the piston and the bore of the cylinder, and the pressure may be read as frequently as desired. This gives a continuous direct means of observing the conditions existing in the capillary.

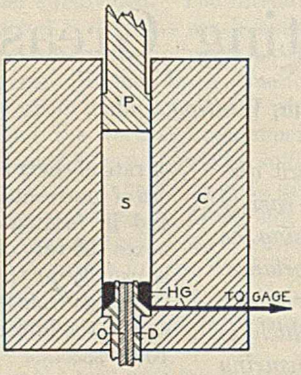

FIGURE 1. PRINCIPLE OF CONSTANT-SHEAR VISCOMETER

The following definite advantages were expected and all have been realized when pressures were determined on the mercury bed:

1. Passage of air bubbles and grease lumps can be detected and the data interpreted accordingly.
2. A large number of observations at equilibrium are possible and are the only readings required during the run.
3. One capillary can be conveniently operated over a large range of efflux rates.
4. No blow holes occur.
5. A source of constant pressure over a large range is not required.
6. The capillaries are readily interchangeable.
7. The pressure differential across the capillary is measured directly.

When the rate of shear is to be increased by reducing the radius of the capillary, the pressures required to produce the specified rate of flow increase very rapidly. This, coupled with the fact that plugging of the capillary causes the rapid development of high pressures, necessitated rugged construction. The design was for 20,000 pounds per square inch (1400 kg. per sq. cm.) on the piston, and pressures of that magnitude have been developed in use.

As shown in Figure 2, a synchronous motor, *A*, drives an 8-speed transmission, *B*, which in turn drives a pair of worm gears, *C*, functioning as nuts drawing forward the screws, *F*, attached to the head, *G*, riding on the rails supported by plates *D* and *E*. The piston, *H*, constructed on the Bridgman principle (*3*) is attached to head *G*, and in operation is forced into cylinder *I*, forcing the oil out of cylinder through duct *J*, through pressure block *K* into viscometer *L*, forcing disk *M* downward. The mercury from the bed about capillary *N* moves through duct *O*, then through the pressure block, *P*, to the manometer at *R* until equilibrium is reached. The sample between disk *M* and capillary support *N*−1 is forced out through the capillary, *N*−3 (see small detail). The method of mounting the capillary *N*−3 is shown. The glass capillary, 3, is ground to a shoulder as shown at 2, and cemented into place at 4 in the support, 1. The bottom of the support is threaded so that the whole acts as a bolt to be fastened into position. The top opening in the viscometer is closed by a plug, *X*, consisting of two parts, 1 and 2, separated on the flat face by a rubber washer. The viscometer is in a thermostat, *V*, controlled by mercury regulator *T*. The bath liquid was thoroughly agitated. Oil was first used as the liquid, but this was found to be unsatisfactory. A 15 per cent soluble oil emulsion was used with excellent results. The heat transfer was satisfactory, and no corrosion of the steel occurred.

The pressure blocks, *K* and *P*, are constructed so that gages, *S*, and manometers both function with the Bridgman plug in the back position, while only the gages function when the plug is in the forward position. The plugs are operated by two valve wheels as shown *Q*.

A detail, *W*, of the Bridgman tube connections is shown. The block has a duct, 3, a plain portion, 1, into which 4 is fitted, and a threaded section, 2, to hold plug 8. Between head 4 and plug 8, two copper washers, 6, and a rubber washer, 7, are placed. Tension on the rubber seal is furnished by plug 8. When pressure is built up in the system, it applies to the full end surface of 4, producing a force which is transmitted to the rubber washer, 7, and causing pressures higher than the internal pressure, thus maintaining a seal. For further comments on Bridgman's developments in high-pressure construction, see his original discussion (*3*).

No trouble of any kind has been experienced with the seals. The system is absolutely tight. The eight speeds of the piston differ by approximately equal logarithmic steps, making it possible to cover an extremely large range in rate of shear with a given capillary on one sample. The speed of the piston covers the entire practical experimental range, since the time required for a full stroke for the highest speed is 4 minutes, and for the lowest, 6 days. Each one of the equilibrium pressures was determined in ascending order, so that the manometer readings might be obtained without

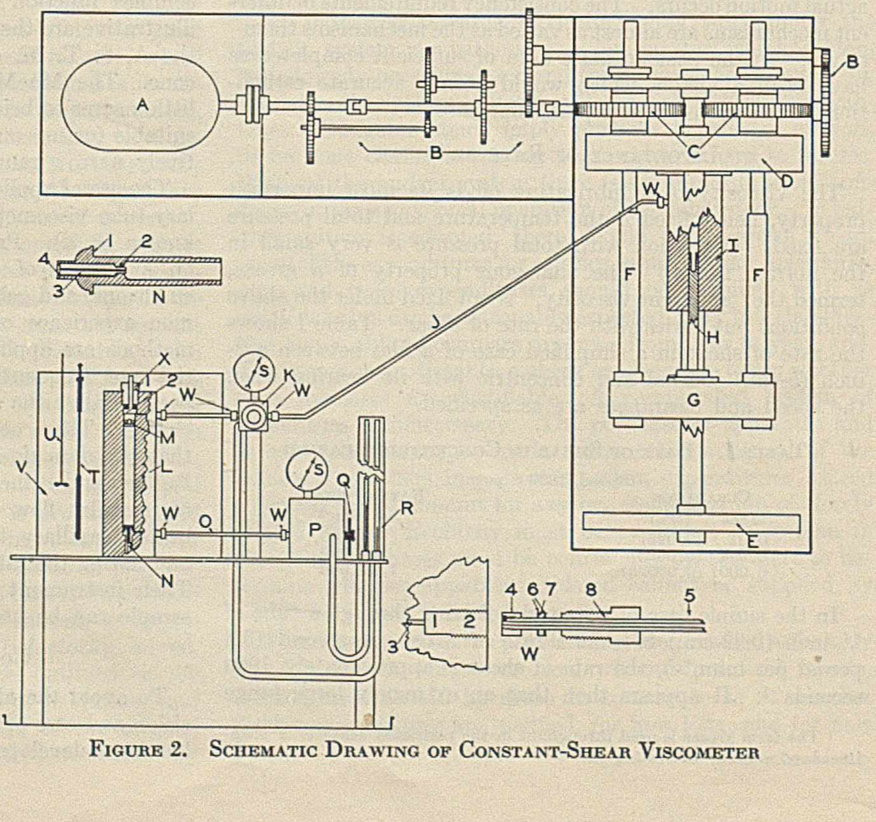

FIGURE 2. SCHEMATIC DRAWING OF CONSTANT-SHEAR VISCOMETER

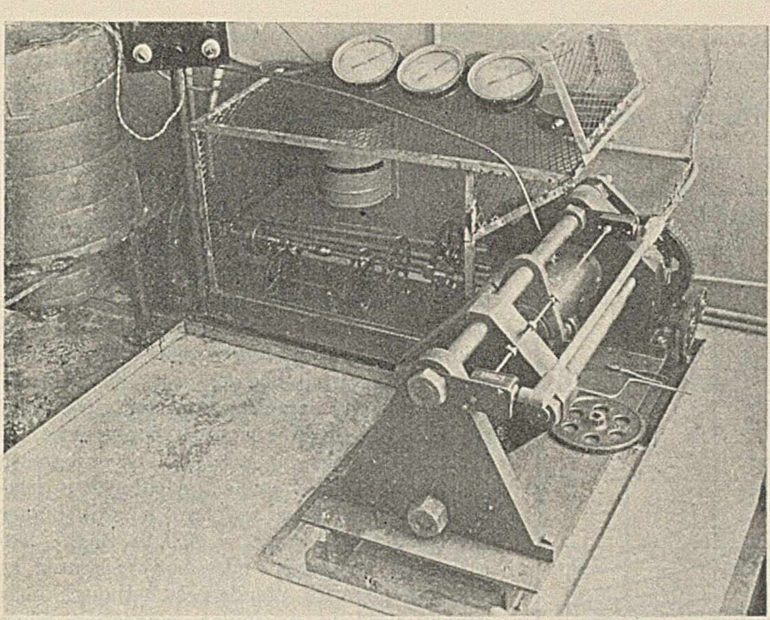

Figure 3. Transmission and Press in Final Assembly

disturbing the mercury system. When the pressure became too high for the manometer, it was blocked, and the proper gage was used.

Method of Calculating and Corrections—It is unnecessary to give in detail the mathematics used. The apparent viscosity is the value calculated from Poiseuille's equation, which, when analyzed as shown, gives the stress at the wall and the rate of shear:

$$\eta_\alpha = \frac{\pi P R^4}{8LV/t} = \frac{\dfrac{PR}{2L}}{\dfrac{4V/t}{\pi R^3}} = \frac{F}{S}$$

where η_α = apparent viscosity, poises
P = pressure, dynes per cm.^{2}
R = radius of capillary, cm.
L = length of capillary, cm.
V/t = rate of efflux, cm.^{3} per second
F = stress, dynes per cm.^{2}
S = rate of shear, seconds^{-1}

The symbols are those conventional in the science of rheology. The dimensions required were determined in the conventional manner.

The measurements were entirely in the viscous region. Furthermore, the kinetic-energy corrections were negligible and no correction was made for end effects. Corrections have been made for the capillary head when required.

It was found that, as the pressures increased, a decrease in the viscosity of oils occurred, owing to the development of heat in the capillary. Sufficient data were obtained to permit corrections for this effect over the lower ranges. The percentage of decrease was proportional only to the pressure observed and amounted to 10 per cent at observed pressure of 300 pounds per square inch (21 kg. per sq. cm.)

The data are given graphically and were obtained on worked greases (60 strokes in the A. S. T. M. grease churn) at one temperature, 77° F. (25° C.).

Apparent Viscosity, a Function of Rate of Shear

Figure 5 is an apparent viscosity–rate of shear diagram of a series of cup greases (calcium soaps of mixed fatty acids in mineral oil) containing the same oil, but varying amounts of soap. Interpolating from this figure, a plot (Figure 6) was prepared which shows lines of constant shear for the relation between the apparent viscosity and the percentage of soap. Figure 7 is an apparent viscosity–rate of shear diagram of the data on two cup greases and a pulp oil (aluminum oleate soap in mineral oil), all containing a paraffin oil of lower viscosity than that in the greases shown in Figure 5.

It must be emphasized that the charts are logarithmic. The extreme variations in apparent viscosity should be noted. For instance, the apparent viscosity of grease VI (Figure 5) was 100,000 poises at a rate of shear of 0.1 second^{-1}, and only 8.4 poises at 100,000 seconds^{-1}, as compared with the oil having a constant viscosity of 1.2 poises, at the fixed temperature 77° F. (25° C.).

The agreement between capillaries (indicating the absence of slippage at the junctions) may be noted from a study of the points for the several capillaries, although there seems to be some evidence that slippage occurred at the lower rates on capillary 3. With the harder greases difficulty was experienced, owing to failure of the mercury to deform the grease, which allowed the latter to enter the gage connection and interfere with the necessary rapid transfer of pressures. The expedient adopted was to read the pressures above the disk *M*, with and without the capillary in position. The use of the first pressure value gave the upper, and the difference gave the lower limit of pressure required to force the grease through the capillary. In later work on other hard greases, the simple expedient was used of increasing the depth of the bed and measuring the pressures directly on the bed. The upper- and lower-limit values are shown by split points in the diagrams, the curve being drawn intermediate in a manner indicated by thorough study of the conditions involved.

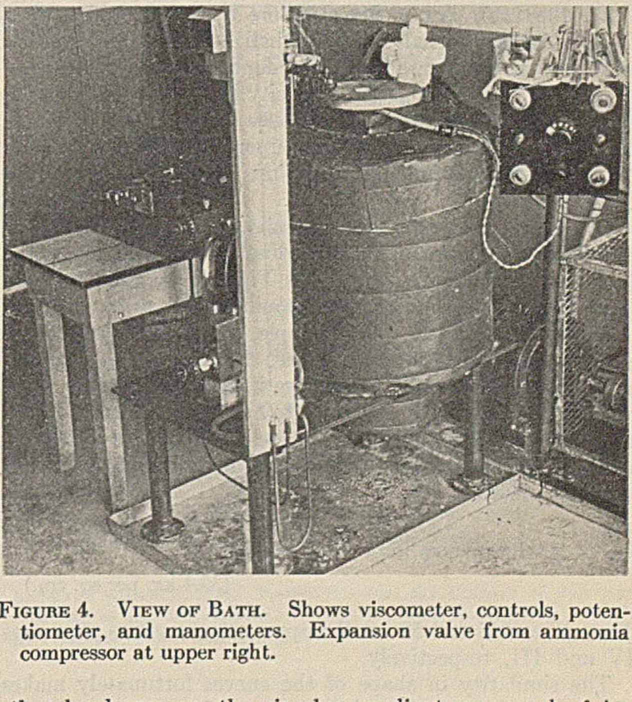

Figure 4. View of Bath. Shows viscometer, controls, potentiometer, and manometers. Expansion valve from ammonia compressor at upper right.

The upper-limit value would be the one obtained in a pressure-viscometer of the fixed-pressure type. The spread between the split points shows the inaccuracies that may be thus encountered and definitely stresses the importance of obtaining the pressure at the entrance to the capillary whenever possible when plastics are concerned. The mercury bed described makes this possible.

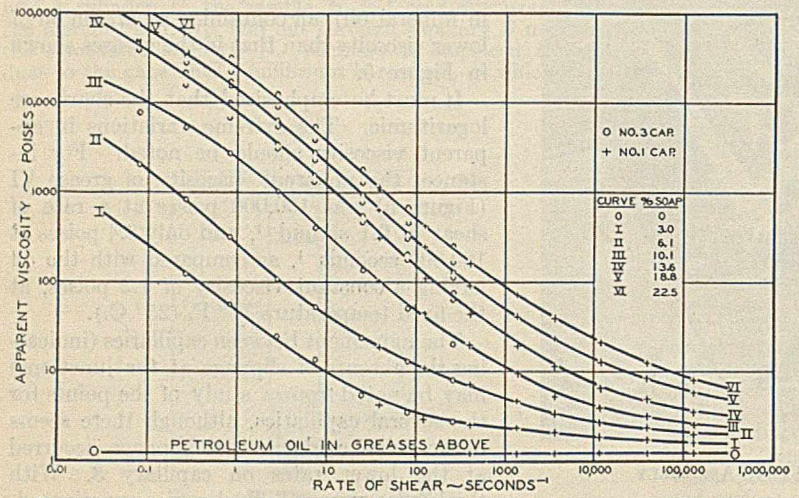

FIGURE 5. APPARENT VISCOSITY–RATE OF SHEAR DIAGRAM OF SERIES OF CUP GREASES

LIMITING VALUE OF APPARENT VISCOSITY

A survey of Figures 5 and 7 serves to demonstrate beyond any doubt that, as the rate of shear increases, the apparent viscosity of the grease approaches some limiting value, higher than, but of the same order of, magnitude as that of the oil in the grease. This may seem obvious, even in the absence of the data, but does not seem to be universally accepted.

To illustrate, certain investigators were surprised to find that, while the initial torque of ball bearings freshly filled with the proper grease was dependent on the consistency—in other words, on apparent viscosity at low rates of shear—the torque and rise in temperature at equilibrium conditions were primarily dependent upon the viscosity of the oil in the grease. These findings are obvious in light of the diagrams given.

In general, the apparent viscosity at low rates of shear governs the dispensing and feeding characteristics of the lubricant, and diagrams such as Figures 5 and 6 may be used to predict what changes would be effected by certain changes in the grease. For example, if a certain piece of dispensing equipment used on grease III (Figure 5) required pressure of 200 pounds per square inch (14 kg. per sq. cm.) at the drum, and it was desired to change to grease IV, and the rate of shear was known to be approximately 100 seconds^{-1}, the pressure required for grease IV could be calculated as follows:

$$\frac{145}{52} \times 200 \text{ lbs. per sq. in.} = 560 \text{ lbs. per sq. in.}$$

(39.4 kg. per sq. cm.)

The values 145 and 52 are the apparent viscosities of greases IV and III, respectively.

The similarity in shape of the curves fortunately makes the accurate estimation of the rate of shear unnecessary in this type of problem where a change between greases of one class is involved. In the above example if the rate of shear should have been either 40 or 400 seconds^{-1}, the pressures required for grease IV would be 630 and 475 pounds per square inch (44.3 and 33.4 kg. per sq. cm.), respectively.

The pulp-oil curve in Figure 7 was included to illustrate that different kinds of soap may produce different trends in the same region. In order to demonstrate that these diagrams represent, as the variation of one property, several characteristics described by the rather vague terms of body, consistency, toughness, tenderness, false body, etc., commonly used in the trade, the following experiments are described: The pulp oil, when placed in a beaker and tilted, will flow very easily, while the No. 0 cup grease will not. This is represented by that portion of the curve at very low rates of shear; e. g., $S = 0.1$. The cup grease is said to have more body. If the two samples are stirred very slowly with a rod, the same will be said to be true to a lesser extent. The rate of shear is somewhat higher; e. g., $S = 1$ to 4. If now the two samples are stirred vigorously, the pulp oil will offer as much, if not more, resistance than the cup grease. The cup grease is said to be tender while the pulp oil is relatively tough. This involves a still higher rate of shear; e. g., $S = 300$ to 1000. Occasionally the term "false body" is used as synonymous with "tenderness," though it is usually used in a similar connection when worked and unworked consistencies are involved.

With the lower and upper ranges of rate of shear fixed by the requirements of use, that grease having the lowest apparent viscosity at intermediate ranges of rate of shear at the temperature of operation will be the most economical of power in bath-type lubrication.

IS THERE ONE GENERAL RELATION FOR EACH KIND OF SOAP?

A close examination of the curves in Figure 5 suggests that they may all be part of one general relation, which is characteristic of each class, and involves, besides the rate of shear, factors characteristic of the oil and soap. It is impossible to set up this relation at the present time, but, as additional data are accumulated, it is expected that such general relations may be evolved which will be characteristic of greases of a given type.

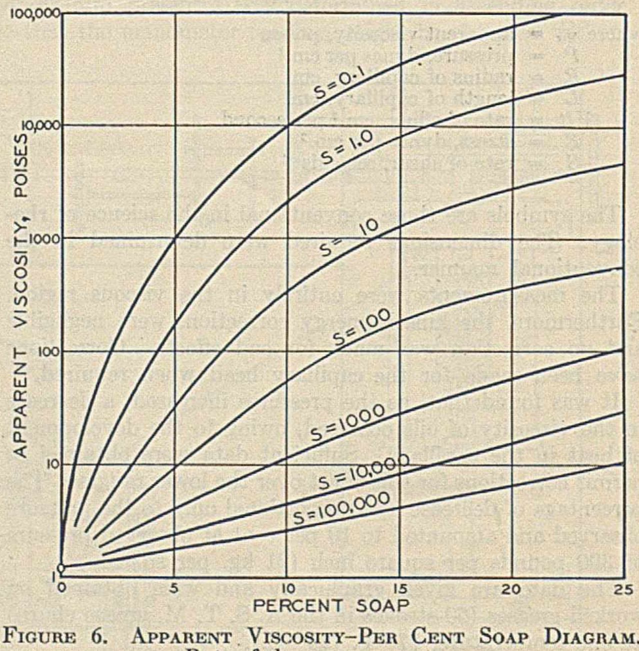

FIGURE 6. APPARENT VISCOSITY–PER CENT SOAP DIAGRAM. Rate of shear as parameter.

A study of the application of equations for plastic flow published by Bingham (*2*), Buckingham (*4*), de Waele (*8*), Williamson (*9*), Reiner (*7*), and others, and the equations presented by Peak and MacLean before the Society of Rheology in December, 1930, but as yet unpublished, has been made, but is too involved for complete discussion at this time. It was not found possible to fit any of these equations to the data. The Williamson equation gave qualitative agreement but could not be fitted accurately. Empirical equations have been found to fit some of the data and will be published later.

Conception of Grease Structure

In the course of this work it was noticed that lime-soap greases, which can be worked to substantially constant consistency in the A. S. T. M. grease churn, could be forced through the capillary of the viscometer without any noticeable additional loss in consistency. This was true even when very high rates of shear were employed. Further, the curves expressing the relation between the apparent viscosity and the rate of shear (see Figures 5 and 7) are obviously members of a definite system which could not well exist if actual severing of elements of the structure occurred. This behavior suggests that the structure of a lime-soap grease may consist of the interlacing of flexible solid members, which may be in themselves deformed or merely separated by the shearing action, but which are not actually ruptured. In other words, any shearing action merely distorts the individual members and reduces the average amount of interlacing, which accounts for the tendency toward working to a constant consistency representing the condition of maximum possible deformation of the members under that particular shearing condition. If, furthermore, the members be elastic, they will tend, after severe deformation, to assume their previous forms. This, in general, explains the fact that a worked grease approaches a limiting value at very high rates of shear—the lowest conceivable limit being at least slightly above the viscosity of the oil—but resumes its worked consistency immediately upon issuing from the capillary. Elasticity of the members surrounded by a viscous medium would also explain the tendency of worked lime-soap greases to increase in consistency on aging.

The common soda-soap greases have much longer and coarser structures than do the lime-soap greases, as is evidenced by their fibrous nature, opacity, and tendency to leak oil in storage. On working, these greases do not give constant penetrations in 60 strokes in the A. S. T. M. grease churn, but work down to very thin, less fibrous, products. It appears then that the individual structural members of these greases differ in size, shape, and structural strength from those of the lime-soap greases and are apparently actually ruptured on working.

Though quite distinct, this conception does have points of similarity with the conception of pseudoplastic flow proposed by Williamson (*9*).

Conclusions

1. A viscometer has been developed which has proved very useful in obtaining data on the flow of greases in capillaries over a very large range of rate of shear. The range reported is from 0.08 to 132,000 seconds^{-1}.

2. The apparent viscosity of petroleum lubricating greases at any given rate of shear increases with increasing concentrations of soap in a manner shown by the figures.

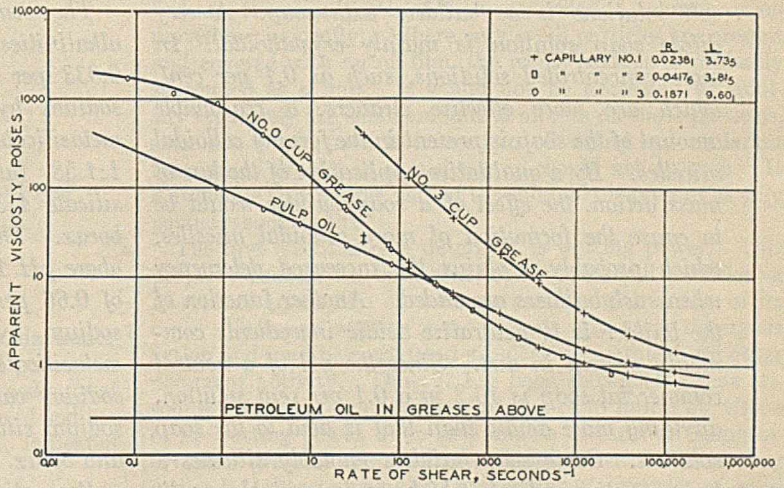

Figure 7. Apparent Viscosity–Rate of Shear Diagram of Several Greases. They contain an oil common to all.

3. The apparent viscosity of greases decreases with increasing rates of shear in a manner characteristic of the particular soap used, approaching in the limit a value higher than, but of the same order of magnitude as, the oil in the grease.

4. The diagrams of the type illustrated may be used to predict the behavior of greases in use.

5. The nature of the apparent viscosity–rate of shear diagrams suggests that one general relation for each type of grease may exist. Additional data are required to substantiate this.

6. None of the equations for plastic flow to be found in the literature appear to be applicable to the data obtained.

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Detergency of Alkaline Salt Solutions

I—Initial and Available Alkalinity

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THE PRIMARY field of detergency of alkaline salt solutions is as builders with soap. A very dilute soap solution is mainly crystalloidal. In more concentrated solutions, such as 0.1 per cent, which are more effective cleaners, a reasonable amount of the soap is present in the form of colloidal micelles. By a qualitative application of the law of mass action, the effect of a soap builder would be to cause the formation of more colloidal micelles, which probably explains the increased detergency when such builders are added. Another function of the builder is to neutralize acidic ingredients commonly present in dirt. Since the pH of a neutral commercial soap is 10.2 in a 0.1 per cent solution, anything more acidic than that is acid to the soap solution. Some soap builders—notably silicates—have negative radicals which, under suitable conditions, are also colloidal.

For the purpose of discussion, the dirt difficult to remove is considered to consist of microscopic and submicroscopic particles coated with oil. These are too small for a detergent solution to displace the oil film and, therefore, behave like oil droplets. Important factors are wetting power, deflocculating power, and emulsifying power. Methods previously used for evaluation of detergency are reviewed.

The compounds studied have decreasing total alkalinities, as shown by pH or C_{OH} values on 0.033 per cent solutions, in the following order: sodium hydroxide, sodium orthosilicate, sodium metasilicate, trisodium phosphate, sodium silicate 1:1.58 (anhydrous), sodium carbonate, sodium silicate 1:3.86 (anhydrous), modified soda, and borax. They have decreasing available alkalinities above pH 10.0, as shown by electrometric titrations of 0.66 per cent solutions, in the following order: sodium hydroxide, sodium orthosilicate, sodium metasilicate, sodium silicate 1:1.58 (anhydrous), sodium carbonate, alkaline trisodium phosphate, sodium silicate 1:3.86 (anhydrous), modified soda, and borax.

For rational comparison of the relative value of soap builders, it is essential that the pH be translated into C_{OH}.

The conclusion reached is that, owing to the necessity of neutralizing acidic dirt, a buffered builder is essential. This rules out sodium hydroxide. The most effective builders, so far as alkalinity is concerned, were found to be sodium orthosilicate and sodium metasilicate in that order of preference.

TO OBTAIN the highest efficiency from soap in commercial use, experience dictates that an alkaline agent be added. In the laundry industry this is known as a soap builder. The widespread use of such builders and the relatively unsatisfactory results when a builder is not used, indicate the importance of such added alkalies.

Commercial soap builders are salts of sodium hydroxide with weak acids. In a few cases the hydroxide itself is used. By far the most common soap builders are the salts with carbonic acid. These are either the commercial normal carbonate, known as soda ash, or variable mixtures with the bicarbonate, known as modified sodas. Other important builders are trisodium phosphate, sodium silicates varying in alkali content, and borax. Caustic soda itself is popular in some sections. Admixed with soda ash it is known as Special Alkali. There are numerous proprietary compounds on the market composed of mixtures of these salts, with or without addition of soap.

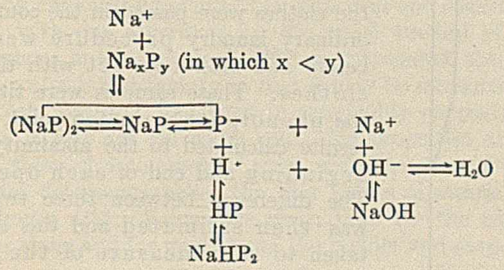
NATURE OF SOAP SOLUTIONS

An aqueous soap solution may be primarily crystalloidal or colloidal, according to concentration. In very dilute solutions it is mainly crystalloidal, but in more concentrated solutions heavily hydrated ionic micelles or aggregates are formed which exhibit the osmotic effect of an ordinary colloid. Although soap in aqueous solution may be called a colloidal electrolyte, this state is in equilibrium with neutral colloidal particles, that is, aggregates of molecules, simple molecules, and simple ions, the amount of each changing with varying conditions.

Soap solutions are alkaline, owing to hydrolysis. For most concentrations the amount of hydroxyl ion present is approximately 0.001 *N*, but in very dilute solutions, although hydrolysis increases, the alkalinity decreases. Even in the presence of excess fatty acid over that equivalent to the alkali, a soap solution remains alkaline so that the other product of hydrolysis must be an acid soap, separating as a finely suspended solid. Excess alkali remains almost entirely in the free condition, showing that basic soaps are not formed. The degree of hydrolysis increases rapidly as the homologous series of fatty acids is ascended. Under laundry conditions hydrolysis occurs to the extent of about 10 per cent. An acetyl sulfonic acid soap, in which hydrolysis is impossible, behaves in most respects like potassium stearate, so that the major properties of soap solutions are believed to be due to the soap itself rather than to any products of hydrolysis.

The law of mass action may be assumed to hold qualitatively in soap solutions, since the addition of common ions to the solution has the effect of producing more colloidal ionic micelles. Such an effect has been obtained experimentally, although the stages which may occur in going from the ionic to the colloidal condition are problematical. When a common ion is added to an ordinary salt solution, the effect may be followed semi-quantitatively, and, since the cause and effect are similar in colloidal solution, parallel equilibria are suggested.

The following representation of the equilibrium in a sodium palmitate solution is intended to indicate as many of the factors concerned as possible. Sodium palmitate is selected for illustrative purposes. The reactions and equilibria with the oleate and stearate are believed to be parallel. In a sodium palmitate solution the negatively charged palmitate cluster contains more than simple palmitate ions. The free fatty acid combines with sodium ion or soap molecules to some extent, forming acid soaps of varying composition which may coëxist in solution with free sodium hydroxide:



$$\begin{array}{lllll}
 & \mathrm{Na^+} & & & \\
 & + & & & \\
 & \mathrm{Na_xP_y}\ \text{(in which } x < y) & & & \\
 & \rightleftharpoons & & & \\
\mathrm{(NaP)_2} \rightleftharpoons & \mathrm{NaP} \rightleftharpoons & \mathrm{P^-} & + & \mathrm{Na^+} \\
 & & + & & + \\
 & & \mathrm{H^+} & + & \mathrm{OH^-} \rightleftharpoons \mathrm{H_2O} \\
 & & \rightleftharpoons & & \rightleftharpoons \\
 & & \mathrm{HP} & & \mathrm{NaOH} \\
 & & \rightleftharpoons & & \\
 & & \mathrm{NaHP_2} & &
\end{array}$$

The ionic micelle is thought to contain some colloidal undissociated soap, so that the micelles of sodium and potassium soaps are not identical as they would be if made up simply of the negative ion. A formula for the ionic micelle of sodium palmitate may be written $(NaP)_x \cdot (P^-)_n \cdot (H_2O)_m$, indicated above as Na_xP_y $(x<y)$.

The addition of sodium hydroxide as such, or as the product of hydrolysis of a salt, drives back the ionization of both sodium palmitate and water, and the whole equilibrium changes in the direction of forming more colloid. The detergent action of a solution is demonstrably improved by increase in the colloidal material present, presumably because it serves as a protective colloid in stabilizing the suspension of particles of soil. Since hydrolysis detracts from these properties, it is common laundry practice to add materials which will decrease the amount of hydrolysis. When such alkaline materials are not used, the slight amount of alkalinity in the soap solution is neutralized immediately by acidic materials present in the dirt, so that the equilibrium is displaced in the other direction, and the colloidal properties of the solution are decreased.

While the chief purpose of adding alkali in laundry practice is to increase the washing power of the soap, the salts employed also have detergent properties of their own, using the term in a broad sense. It has been the purpose of this study to compare solutions of the salts used as laundry soap builders, first with respect to their alkalinity as soap builders, and second with respect to their detergency as supplementary washing materials in addition to soap.

DETERGENT ACTION

The removal of dirt from soiled fabric or from other surfaces is a complex procedure involving a number of different factors, both physical and chemical. In the study of the efficiency of any one detergent or combination of detergents, it is desirable to determine the nature of those factors, and then to examine the detergent with respect to each separate factor.

First, the nature of the dirt to be removed must be considered. Since it is impossible to subject dirt as it exists on soiled fabric to chemical analysis, its exact nature must remain a matter of conjecture. A number of investigators (*1*, *4*, *12*) have assumed the existence of "clean" dirt, that is, small solid particles, as of carbon black or graphite, which become embedded in the soiled surface and are free of grease. It is probably true that small solid particles of dust, soot, etc., do become embedded in soiled fabric, but it is more probable that the majority of these particles are covered with a light film of greasy matter which would cause the particles to adhere to the soiled surface. A large part of the average dirt film probably consists of grease, varying according to the manner in which the surface was soiled. This grease is composed of unsaponifiable oil, saponifiable oil, and free fatty acids in varying proportions.

When solid particles covered with an oil film are of comparatively large size, the oil film is first displaced and emulsified and the clean particles then suspended in solution or removed mechanically. Where very small particles are present and covered with an oil film, the whole particle is probably suspended as a unit. It would not be necessary to emulsify separately the small amount of oil film on these particles, since the whole particle incased in oil would not be larger than an oil droplet in emulsion, and would act as such. It is probable that a large part of the solid dirt is present as tiny particles such as this.

The first essential of a detergent is wetting power. This property enables the detergent to wet the small particles or to replace an oil film on a larger particle with a film of its own. Thorough wetting must precede any other detergent action and may be considered a function separate from other detergent activity. Thus, it has been shown (*15*) that trisodium phosphate can remove greases from fabric by virtue of its wetting power when it is unable to form an emulsion of those greases. A detergent should have deflocculating power in order to break up aggregates of particles of solid dirt. It should also have emulsifying power in order to disperse the oil or oil-covered dirt particles. Finally, alkalinity should be present in the detergent solution in an amount sufficient to neutralize the free acidity of the dirt.

METHODS OF DETERMINATION OF DETERGENCY

Various methods of measuring the efficiency of various detergents have been proposed and tried out. It has been very difficult to find any one method that would take into account all of the factors involved, so that most of the work in this field has been carried out on one or another of the separate functions of a detergent. The different methods have been summarized by McBain (*11*) as follows:

(1) Measurement of surface tension against air by capillary tubes or by drop numbers or by bubbling or by measuring the amount of froth produced under definite conditions.

(2) The measurement of surface tension against oil or paraffin oil or benzene by drop numbers or measurement of emulsification.

(3) Measurement against carbon or other powders by measuring rate of sedimentation or protective action in filtration.

(4) Protective action as measured by gold numbers.

(5) Direct-washing experiments with specially soiled clothes under controlled conditions of true temperature and concentration.

Measurement of surface tension against air has been used by many investigators because of its ease and simplicity. This value, however, cannot be assumed to represent the wetting action of the detergent against greasy dirt since the interface in that case is between the detergent solution and an oil. The interfacial tension of a solution against air may determine the amount of suds which that solution will produce, but the actual value of suds in washing is open to question. Measurement of interfacial tension against a liquid immiscible with water should give results more closely related to actual washing power. Determination of this value by the drop-number method was first used by Donnan (*3*).

Measurements of the power of suspending inert dirt by filtering suspensions of carbon black (*12*), or by shaking clean

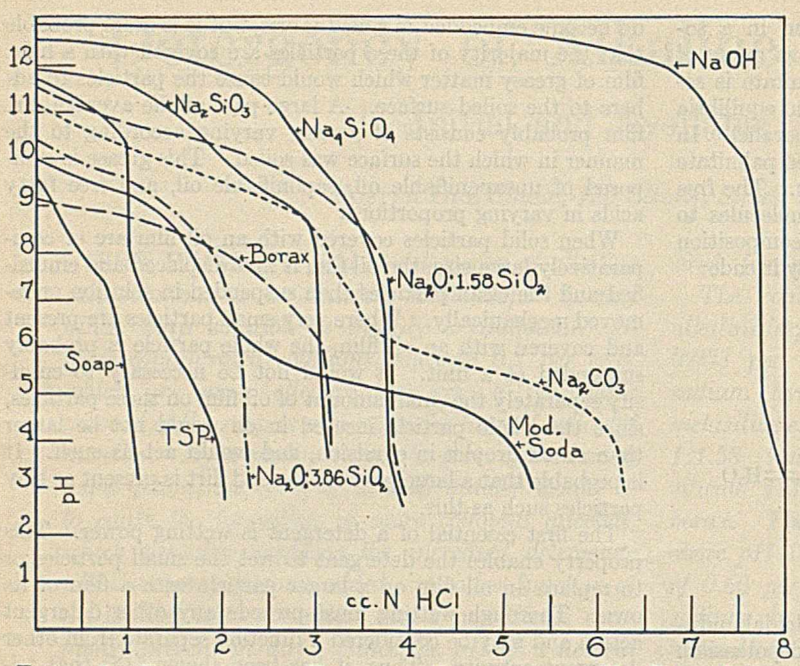


FIGURE 1. ELECTROMETRIC TITRATIONS EXPRESSED AS pH. Soap solutions (0.66 per cent) and common soap builders at 25 ° C.

graphite with a soap solution and observing an end point of suds between froth and solution (*1*) gave variable results. A more successful method of this type is that developed by Fall (*4*) in which he suspended manganese dioxide in a soap solution, and then determined the amount of manganese dioxide in a fixed volume of stable suspension by titration. This assumes that clean manganese dioxide is representative of the properties of normal dirt.

The gold-number method has apparently been employed by only one investigator (*5*). According to this method the minimum quantity of colloid required to protect a fixed volume of red-gold sol from precipitation on the addition of a definite amount of sodium chloride was determined. Protective action toward red-gold sol is not very closely related to deflocculating or emulsifying power.

Direct-washing tests on specially soiled fabrics are described by Heermann (*7*). Recent tests with the same type of procedure under carefully controlled conditions have been carried out by Rhodes and Brainard (*13*). The difficulty encountered with this method has been in finding a suitable artificial soiling material, and a variety of substances have been tried for the purpose (*8*). A subcommittee of the American Oil Chemists Society is working on the development of a standard method for direct washing tests at the present time (*2*, *9*, *14*). Their soils are carbon black and burnt umber. Tests of this kind under carefully defined conditions are valuable as a correlation of data obtained by the other methods.

In this study the alkaline properties of the salt solutions have been measured, first in order to show their effectiveness in repressing hydrolysis of soap solutions, and also as an indication of their detergency. For determination of wetting power, the measurement of interfacial tension against an oil has been chosen as the most accurate and convenient method. Results from these determinations may also be considered as indirectly indicating the emulsifying power. For direct determination of emulsifying power, a method has been devised wherein the ability to suspend small particles coated with oil is measured. Finally, practical washing tests with a specially constructed washing machine have been carried out as a check on the results obtained by the other determinations.

ALKALINITY OF SOAP-BUILDER SOLUTIONS

In order to substantiate the theory that it is necessary to neutralize acidic materials in solid fabric, tests were made in a power laundry on the wash solutions in normal use. A sodium carbonate builder was used in this laundry in conjunction with the soap. Samples from the first four wash waters through which the clothes were passed in the course of the ordinary laundry procedure were taken before and after contact with the soiled clothes. These samples were titrated to the phenolphthalein end point, and the results calculated to the alkalinity at the beginning and end of each operation. The difference between these two values was then estimated and this difference taken to be a measure of the acidity neutralized. The amounts of acidity neutralized per liter in the first four washes were as follows:

	Moles per liter
First wash	0.0050
Second wash	0.0024
Third wash	0.0022
Fourth wash	0.0009
Total acidic materials neutralized	0.0105

This is not an accurate measure of the actual amount of acidic materials present in the dirt of an ordinary laundry load, since the washing solution used in this laundry cannot be assumed to have entirely removed all such materials. These tests show definitely, however, that there is a considerable amount of acid to be neutralized by the detergent solution under laundry conditions. One purpose of using an alkali in addition to soap is therefore evident.

Since the salts used as soap builders are uniformly salts of strong bases and weak acids, the alkalinity produced in solution is buffered. The concentration of alkali when the salt is first dissolved does not represent the total alkali available for reaction with acid, since further hydrolysis occurs as reaction proceeds. In measuring the alkalinity of these salts, therefore, two separate factors must be considered—the initial concentration of hydroxyl ion and the total amount of alkalinity available for reaction. The initial alkalinity has been measured by pH determinations and the total alkalinity by electrometric titrations.

Soap concentrations, as ordinarily used in the power laundry, vary between 0.1 and 0.15 per cent. For sodium palmitate this corresponds to 0.0036–0.0054 *N*, and the normalities are very nearly the same for sodium oleate or stearate. The amount of builder used in proportion to the soap generally varies according to the strength of the builder. In general, a strong builder, referring to a salt giving alkalinity buffered at a relatively high level, is used in equal amounts with soap, a moderately strong one in the proportion of 2 parts of soap to 1 of builder, and a weak one in the proportion of 3 parts of soap to 1 of builder. This indicates that a strong builder is considered to have sufficient detergent properties so that it may replace some of the soap. The weakest concentration, a 0.033 per cent solution, has been chosen for these determinations as being most representative of general laundry practice and as the fairest basis for comparison.

Solutions of the following salts, having approximate compositions as noted, were prepared:

Sodium metasilicate, $Na_2O:SiO_2:9H_2O$; sodium silicate, $Na_2O:1.58SiO_2$ (anhydrous); sodium silicate, $Na_2O:3.86SiO_2$ (anhydrous); trisodium phosphate, $Na_3PO_4:12H_2O$; sodium carbonate, Na_2CO_3; modified soda, $Na_2CO_3:NaHCO_3$; borax $Na_2B_4O_7:10H_2O$.

The pH values of these solutions at 25° C. are presented in Table I. The values for similar solutions of sodium hydroxide and of sodium oleate are included to show comparative figures for a highly alkaline material and for soap alone. Sodium oleate was chosen as the standard soap for several reasons. It can be prepared in a substantially pure condition by mixing chemical equivalents of oleic acid and sodum hydroxide, with due allowance for the small amount of free hydrocarbons in the oleic acid. When so prepared, the solubility in water is satisfactory so that it may be measured out from a cold solution, and even in reasonably concentrated solutions it will not gel when cold. Its properties are, in general, those of a commercial soap, with due allowance for its greater detergency below the titer values of stearic acid and palmitic acid. Values are given both for the builder solutions alone and for mixtures of the builder and soap.

TABLE I. INITIAL CONCENTRATION OF ALKALI IN SOLUTIONS OF BUILDER

(At 25° C., with and without soap)

	0.033% SOLN. OF BUILDER		SAME + 0.1% SOLN. OF SOAP	
	pH	C_{OH} ($\times 10^{-3}$)	pH	C_{OH} ($\times 10^{-3}$)
Sodium hydroxide	11.85	7.10	11.9	7.94
Sodium metasilicate	11.2	1.60	11.3	1.99
Alkaline trisodium phosphate	10.8	0.63	11.1	1.26
Sodium silicate 1:1.58 (anhydrous)	10.7	0.50	11.0	1.00
Sodium carbonate	10.65	0.45	11.0	1.00
Sodium silicate 1:3.86 (anhydrous)	10.1	0.12	10.4	0.25
Modified soda	10.0	0.10	10.3	0.19
Borax	9.35	0.022	9.8	0.063
Sodium oleate	10.2	0.16	...	...

While pH values are a convenient form of expressing hydrogen-ion concentration, these values are apt to be misleading for comparative purposes. The pH value is a logarithmic function so that the actual difference in concentration of hydroxyl ion, represented by 0.1 unit of pH, is not constant. Thus the difference in actual concentration of hydroxyl ion between a solution of pH 10.1 and one of pH 10.2 is less than one-fourth as much as the difference between a solution of pH 10.8 and one of pH 10.9. For comparative purposes, therefore, the pH values have been calculated to C_{OH} values, assuming pH 7.0 at 25° C. = C_{OH} 1.0×10^{-7}, and these are included in Table I. Calculation to C_{OH} in this way shows the wide difference between all of these salts and sodium hydroxide, which is not so clearly shown by pH values.

The electrometric titrations shown in Figure 1 illustrate the behavior of the builders on reaction. These titrations were carried out with the hydrogen electrode, and, since 0.033 per cent solutions are so dilute as to give results of questionable accuracy, the solutions were made up to a concentration of 0.66 per cent. While the actual concentrations of hydroxyl ion were higher than those occurring in laundry practice, the results serve for comparative purposes. Figure 2 gives the corresponding results in terms of C_{OH}. The curve for sodium hydroxide could not be shown in that case, as it is so far off the scale.

The author believes that the usefulness of a soap builder in the wash wheel continues only so long as it maintains an alkalinity in the solution greater than that corresponding to a pH of 10.0 or a C_{OH} of 0.0001. This is based on the fact that the soap solution alone has a pH of 10.2, so that, to be effective, the builder should not decrease the alkalinity. A comparison of the different builders after reaction with varying amounts of acid is shown in Table II in terms of C_{OH}. According to this table, sodium silicate (1:1.58) would retain its effectiveness against acidity for the longest time in the wash wheel, although the concentration of alkali produced by it is never as strong as that produced under the same conditions by metasilicate. This comparison is not strictly correct because silicate (1:1.58) and silicate (1:3.86) were taken on an anhydrous basis. Allowing for that, sodium metasilicate is by far the best soap builder of those considered up to this point, aside from sodium hydroxide.

TABLE II. CONCENTRATION OF HYDROXYL ION

(After reaction with varying amounts of acidic materials from fabrics)

	MOLES ACIDIC MATERIAL REMOVED			
	0.0005	0.001	0.0015	0.002
Sodium metasilicate	0.008	0.007	0.0043	<0.0001
Alkaline trisodium phosphate	0.003	<0.0001	....	....
Sodium silicate (1:1.58, anhydrous)	0.002	0.0006	0.0002	0.0001
Sodium carbonate	0.0006	0.0001	<0.0001	....
Sodium silicate (1:3.86, anhydrous)	<0.0001	....	....	....
Modified soda	<0.0001	....	....	....
Borax	<0.0001	....	....	....

Caustic soda is the strongest alkali of the materials used as builders, and it is popular for that reason in some sections. Its chief disadvantage is the harmful effect on fabrics that results when it is not thoroughly neutralized or rinsed out before drying. It must also be used carefully, since only very dilute solutions are safe for the cleaning of fabrics. Any danger to fabrics is greatly reduced when buffered salts are employed, and materials of this sort are preferred by many laundries even when their effectiveness is not as great, as in the case of modified soda. The ideal soap builder would be one which would be potentially strongly alkaline, but at the same time buffered so as to yield all of its alkaline strength only on reaction. From consideration of the three grades of sodium silicate examined in comparison with the other salts, it seemed that a silicate with the highest possible ratio of Na_2O to SiO_2 would most nearly approach this specification.

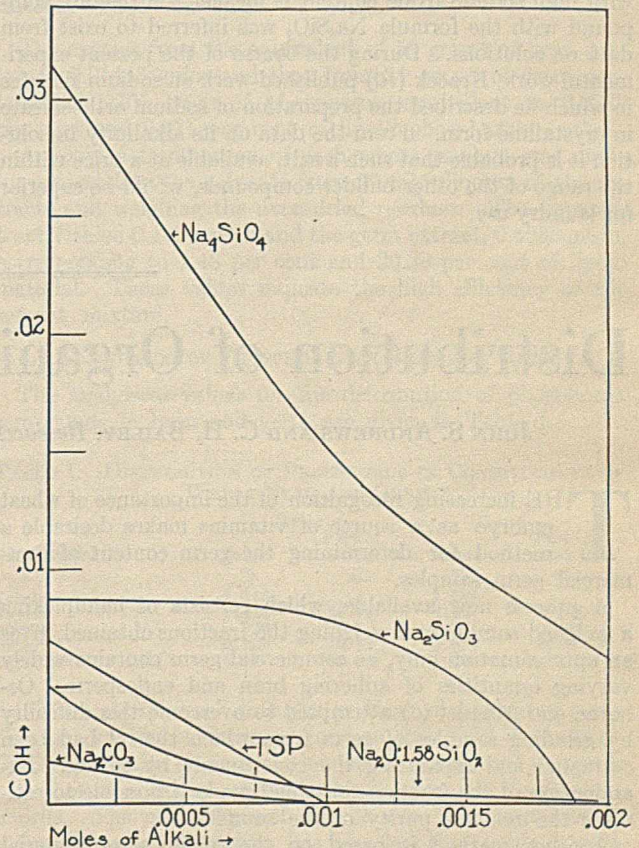


FIGURE 2. ELECTROMETRIC TITRATIONS EXPRESSED AS C_{OH}. Soap solutions (0.66 per cent) and common soap builders at 25° C.

From work of Harman (*6*) it is indicated that the orthosilicate, having a ratio of Na_2O to SiO_2 of 2:1, exists in solution, although he was unable to obtain it as a dry salt. Since the Na_2O content in this compound is higher than in the metasilicate, the alkaline strength would be greater although buffered in the same way. Harman's results also showed that the pH of a solution of the $2Na_2O:SiO_2$ salt was only slightly higher than that of a solution of the 1:1 ratio salt, so that the initial concentration of hydroxyl ion would not be dangerously high. Sodium orthosilicate therefore appears to be a material which will furnish practically the greatest amount of alkalinity compatible with safety for use as a soap builder.

A solution corresponding to a 0.033 per cent solution of sodium orthosilicate was made up from sodium metasilicate and sodium hydroxide, and its alkalinity measured in the same way as with the other solutions. The initial pH was found to be 11.3 as compared with 11.2 for sodium metasilicate. The corresponding C_{OH} values are 1.99×10^{-3} for orthosilicate, as compared with 1.60×10^{-3} for metasilicate. The titration curve is included in Figures 1 and 2 for a 0.66 per cent solution, and shows the distinct superiority of this solution over that of the metasilicate in total alkalinity above the pH 10.0 level.

While a considerable volume of data has been published on sodium silicates, the information available on the silicates with high sodium oxide content is meager. A definite compound with the formula Na_4SiO_4 was inferred to exist from data on solutions. During the course of the present experimental work, Kracek (*10*) published work on sodium silicates in which he described the preparation of sodium orthosilicate in crystalline form. From the data on its alkalinity in solution it is probable that such a salt, available at a price within the range of the other builder compounds, would be superior for laundry use.

Conclusion

A primary consideration in the selection of a salt to be used for increasing the detergency of a soap solution is the alkalinity produced by it on hydrolysis. Comparison must be made on the basis of the total alkaline strength available after reaction has proceeded to some extent, as well as on the basis of the initial hydroxyl-ion concentration before reaction. Based on the consideration of both of these factors, a sodium silicate having a $Na_2:SiO_2$ ratio of 2:1 would be the most effective addition agent. Aside from that, the most efficient material available on the market is sodium metasilicate, having a $Na_2O:SiO_2$ ratio of 1:1.

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Distribution of Organic Phosphorus in Wheat

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THE increasing recognition of the importance of wheat embryo as a source of vitamins makes desirable a method for determining the germ content of commercial germ samples.

A process now available, which consists of handpicking a weighed sample and weighing the fractions obtained, gives an approximation only, as commercial germ contains widely varying quantities of adhering bran and endosperm. Osborne and Mendel (*6*) attempted to overcome this difficulty by grinding samples of germ from which the oil had been extracted and separating the constituents by sifting. Examination of the fractions obtained made it possible to estimate the relative purity of the samples.

Another method is based on the quantity of material removed by extraction with ether. Wheat embryo contains as much as 16 per cent of these ether-soluble substances. Consequently samples having materially smaller proportions may be suspected of containing parts of the wheat kernel other than the germ. This method, however, gives only approximate values, owing to the variability of the crude fat (ether extract) content in different types of wheat embryo. In addition, the presence of bran, which contains appreciable amounts of ether-soluble material, detracts from the reliability of the results.

In order to develop a method that will permit a more accurate estimation of the purity of germ samples, several of the constituents of bran, germ, and endosperm have been quantitatively determined. This has led to an extensive consideration of the phosphorus-containing compounds in the various portions of the wheat berry. These compounds include phytin, phospholipoids, nucleic acid derivatives, and the inorganic phosphorus combinations. Phytin and phospholipoids are the subject of this preliminary paper.

The literature on the analysis of phosphorus-containing materials in wheat products, particularly bran, is extensive. J. B. Rather has shown that the phosphorus in the phytin accounts for 88 per cent of the total phosphorus in bran (*7*). Averill and King (*1*) report an equally high value for the phytin content of bran.

The phospholipoid content of various wheat products also has been widely studied. Sullivan and Near (*8*), who investigated the phosphorus content of ether and ether-alcohol extracts of several mill products, found a very small amount of lipoid phosphorus in proportion to the total phosphorus. These investigators point out the fallacy of applying the term "lipoid" to ether extraction residues, showing that ether alone does not remove all the lipoid materials. Guerrant (*3*) used a microcolorimetric method to study the phospholipoid content of seeds. His results show the efficiency of various mixtures of alcohol and ether for the removal of phospholipins.

Phytin Content of Bran and Embryo

Coarse fifth break "scalpings" which had been passed through the bran duster and represents the purest product that can be commercially prepared was used in these studies. The analysis for starch (official A. O. A. C. method) placed the quantity of this constituent at 11.3 per cent, which is considered to be equivalent to about 16 per cent of endosperm material. This bran was ground to less than 40-mesh size and dried for 24 hours at 60° C. at a pressure of 3 mm.

The germ used was obtained in the form of whole, unflaked wheat embryos and was specially purified in the laboratory. After extraction with water, the settled residue was found to contain almost undetectable quantities of bran. Staining with iodine and examination under the microscope indicated a very small proportion of endosperm material. This germ, the estimated purity of which was placed at between 90 and 95 per cent, was ground to pass a 40-mesh sieve and dried in vacuum at 60° C.

Of several methods available for the determination of phytin, that proposed by Heubner and Stadler as modified by Averill and King (*1*, *4*) seemed most satisfactory. A hydrochloric acid extract of the product under examination was titrated with a standard solution of ferric chloride, resulting in the formation of an insoluble precipitate of iron-phytic acid complex. Addition of an excess of the ferric chloride was indicated by ammonium thiocyanate. The formation of a precipitate hinders an accurate determination of the end point. Accordingly, a modification to give a check on the values obtained was introduced. The phytin precipitate was removed by filtration and washed thoroughly and its phosphorus content was determined. The two values thus obtained are in satisfactory agreement. The procedure was as follows:

> Extract 25 grams of bran and 30 grams of germ by shaking for 3 hours with 2 per cent hydrochloric acid solution (25 ml. of acid solution for each gram of material). Centrifuge, to throw down the suspended material, further clarify the extract by filtering through Filter-cel. Free the Filter-cel from traces of iron, which would react with the phytin in the extract, by treating with concentrated hydrochloric acid, washing free of chloride, and drying at 100° C. in a vacuum oven.
>
> Take 25 ml. aliquots of the bran extract for analysis and dilute to 85 ml. with water. Add 1 ml. of 3 per cent ammonium thiocyanate solution and carry out the titration by slow addition from a capillary buret of the standard ferric chloride solution (containing 0.001954 gram of iron per ml. of solution). When the end point is nearly reached stop the titration and let the solution stand for 5 minutes. Filter off the precipitate. The titration is concluded without the obscuring effect of the bulk of the precipitated phytic acid.

Titration values ranging from 6.0 to 6.13 ml. of ferric chloride solution were obtained from six replicate determinations. These correspond to 1.39 to 1.42 per cent phytin phosphorus, or 4.93 to 5.04 per cent (average 4.99 per cent) phytin in bran.

Germ extract samples of the same size were similarly analyzed. Four replicate determinations gave values ranging from 2.35 to 2.45 ml. of ferric chloride. These are equivalent to 0.545 to 0.568 per cent of phytin phosphorus, or 1.93 to 2.02 per cent (average, 1.98 per cent) phytin in germ.

The phytin precipitate from 25 ml. of either the bran or the germ extract is too small for a macro phosphorus determination. Accordingly, 75 ml. aliquots of the bran extract were diluted to 200 ml. and the phytin was precipitated by the addition of a slight excess of ferric chloride solution. The precipitates were filtered off and thoroughly washed with 0.05 per cent hydrochloric acid solution, after which the organic material was destroyed by the Kjeldahl method. Phosphorus determinations were made by twice precipitating with ammonium molybdate and weighing as magnesium pyrophosphate. The phytin precipitate was found to contain 1.415 per cent phosphorus. The filtrate and washings were evaporated and the organic material was decomposed. The phosphorus content was 0.155 per cent. In the same way aliquots of the original bran extract were found to contain 1.61 per cent phosphorus. The phosphorus content of the original bran was 1.646 per cent.

Analysis of the germ and 200 ml. of the germ extract gave the following values: total phosphorus in germ, 1.244 per cent; phosphorus in extract, 1.004 per cent; phytin phosphorus, 0.597 per cent.

Lipoid Phosphorus

The choice of an extracting medium for the removal of the lipoid phosphorus was based on Guerrant's results (*3*). Accordingly, 25 ml. of a mixture of 80 per cent absolute alcohol and 20 per cent anhydrous ether were employed for each gram of material under examination. The procedure was as follows:

> Extract 120 grams of finely ground and dried bran and 60 grams of similarly treated germ with the alcohol-ether mixture by intermittent shaking for 48 hours. Clarify the resulting extracts by centrifuging. Take aliquots for analysis. Prepare the phosphorus-containing solutions for the determination by evaporation of the solvent and destruction of the organic material by kjeldahlization.

The extract from the equivalent of 50 grams of bran contained 0.01415 gram and that from 24 grams of germ contained 0.01705 gram of phosphorus, equivalent to 0.0283 per cent and 0.071 per cent of lipoid phosphorus.

A lipoid determination of each wheat product was made by evaporating the solvents from 50 ml. aliquots of the extracts and weighing the oven-dried residues. The bran extract yielded 0.1496 gram and the germ extract, 0.4056 gram, corresponding to 7.48 per cent and 20.28 per cent of lipoid material. These values indicate the high efficiency of the solvent mixture.

Discussion of Phosphorus in Bran and Germ

The analytical values for the distribution of phosphorus compounds in bran and germ are given in Table I.

Table I. Distribution of Phosphorus in Constituents of Wheat Bran and Germ

	Bran		Germ	
Phosphorus	Found	Part of total P	Found	Part of total P
	%	%	%	%
Total	1.646	...	1.244	...
Phytin	1.415	85.96	0.597	47.98
Lipoid	0.028	1.7	0.071	5.70
Other	0.203	12.33	0.576	46.3
Extracted by 2% HCl	1.61	97.8	1.004	80.71

"Other phosphorus" includes at least two types of phosphorus compounds, inorganic and nucleic acid derivatives. Collison's results (*2*) indicate low concentrations of inorganic phosphorus in values corresponding to those for lipoid phosphorus. The other type of phosphorus, that contained in the nucleic acid derivatives, has been less thoroughly investigated from the standpoint of quantitative occurrence. Osborne (*5*) first estimated the amount of this phosphorus-containing material in wheat germ by determining the quantity of purine bases produced by hydrolysis. His value, 3.56 per cent nucleic acid, equivalent to 0.317 per cent phosphorus, cannot be applied to the germ sample investigated here, as in all probability Osborne's sample was different. Also there is no evidence that the results of his method accurately express the concentration of nucleic acid derivatives. The absence of a satisfactory method necessitates the omission of analytical data for the nucleic acid phosphorus at this time.

PHYTIN CONTENT OF ENDOSPERM

Although the investigation on the distribution of phosphorus-containing compounds here reported was confined chiefly to the bran and embryo, the phytin phosphorus content of the endosperm received some attention. In their studies on the phytin content of foodstuffs, Averill and King (*1*) included several wheat flours. In some instances they report phytin phosphorus contents as high as 0.36 and 0.346 per cent. Approximately 25 per cent of the ash of commercial patent flours can be considered as phosphorus. Assuming that all the phosphorus is originally combined as phytin, the ash content of these two flours should be approximately 1.4 per cent. This value is several times higher than that (0.40 per cent ±) reported by the manufacturers of the flour in question.

A sample of second middlings, representative of a pure commercial endosperm, examined in this laboratory, contained 0.35 per cent of ash. By titrating an extract, following the method as modified by Averill and King, the amount of phytin present is too small to be detected. Assuming that all the phosphorus present is combined as phytin, nearly 0.32 per cent of phytin should have been found. As the titration method shows the presence of such quantities, it becomes evident that only a very small proportion, if any, of the phosphorus in the endosperm occurs in the form of phytin.

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Dew Points of Paraffin Hydrocarbons

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THE WIDESPREAD domestic and industrial use of the liquefied petroleum gases has made necessary an accurate knowledge of their dew points. The theoretical dew points of such mixtures are easily calculated by use of Raoult's law and other well-known rules. However, until verified experimentally, it is unwise to assign very great accuracy to such theoretical data. This article describes a method for experimentally determining dew points, indicates the accuracy of Raoult's law, and describes a method for representing and calculating dew points of complex mixtures.

THE dew points were determined by either measuring the contraction in volume of the vapor as the temperature was lowered and the pressure held constant, or by measuring the contraction in volume when the pressure was increased and the temperature held constant. In either case, the dew point was indicated by a sudden increase in the rate of the contraction at the dew-point temperature or pressure.

DETERMINATION OF DEW POINTS

The apparatus consisted of a glass bulb containing the sample and surrounded by a constant-temperature bath. This glass bulb communicated with a buret so that volume changes could be detected and the pressure changed at will by a transfer of more or less of the sample from the buret to the bulb. The bottom of the buret was closed by mercury which served as a seal to the buret and dew-point bulb system, and also as a piston for transferring the vapor from the buret to the bulb. The pressure in the bulb was measured by balancing against a known external pressure on the mercury seal.

Figure 1 is a diagrammatic sketch of the dew-point apparatus and auxiliaries. The water or alcohol bath was of about 1 gallon (3.8 liter) capacity and filled with one or the other of these liquids as the temperature required. The temperature of the bath was lowered and maintained by expanding a refrigerant (liquid propane or butane) through the cooling coil contained just within the wall of the bath. The temperature of the vapor within the dew-point bulb was determined by a thermometer placed as shown. This thermometer was either a −40 to +120° F. mercury thermometer, graduated to 1° F., or a −110 to +50° C. toluene thermometer graduated to 1° C. for the first part of the work. During recent work a +30 to +120° F. mercury thermometer graduated to 0.1° F. has been used.

The dew-point bulb was a small Pyrex glass bulb of approximately 10 cc. capacity. The buret was of 3 mm. internal diameter and about 750 mm. in length. The volume of its contents was read on an ordinary meter stick fixed behind the buret. The bottom of the buret was sealed to a rather large U-tube which served as a mercury reservoir and a seal for the buret. Two stopcocks sealed into the side of the U permitted evacuation of the bulb and buret through one, and introduction of the sample through the other. During a test the mercury was always raised above the level of these stopcocks, thereby effectually sealing the sample within the bulb and buret. The right-hand side of the U-tube communicated with a source of constant pressure through a system of valves which were used to vary the pressure as desired. A 2000-mm. mercury manometer and a pressure gage were used to measure the pressure. A high-vacuum connection was made to both right and left sides of the U-tube so that the apparatus could be evacuated preparatory to introducing a fresh sample.

The 100-cc. measuring buret and storage bulb shown at the left of the figure were used in synthesizing samples of known composition from pure compounds. The stopcocks and connecting tubing were so arranged that samples could be introduced to the apparatus without passing through the buret or storage bulb. All the apparatus and tubing coming in contact with the samples were of Pyrex glass.

Rubber tubing was not used because it is very pervious to paraffin hydrocarbons. A non-grease stopcock lubricant should be used when working with the less volatile hydrocarbons, such as isopentane.

The dew-point determinations were easily made after a little practice. Determinations during the first part of the work were made by holding the pressure of the sample at some constant value while the temperature was lowered by steps. Conditions were held constant a short time during each step before a reading was taken. This method is the more difficult since it requires the adjustment of the pressure as well as the temperature after each step. This pressure adjustment is made necessary by the rise of the mercury in the buret during each lowering of the temperature. During recent work, the temperature was held constant and the pressure increased by steps. This procedure is considerably easier than the first, since the temperature can be held constant with very little attention, and all readings concerning the pressure may be recorded without any calculations at the time. The corrections for height of mercury in the buret may be made at any time after the completion of the test. Another advantage of this second method is the fact that readings may be taken immediately after a change in pressure, since pressure equilibrium is obtained almost instantaneously. It is necessary to wait some time for temperature conditions to come to equilibrium when using the first method.

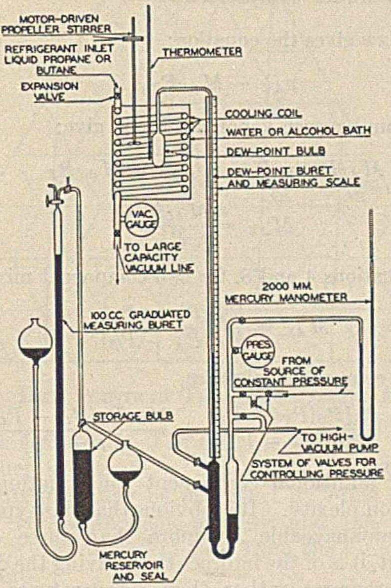

Figure 1. Dew-Point Apparatus

Character of Samples Tested—The samples used in these dew-point determinations were of four types:

(1) Natural samples, such as the commercial grades of liquefied petroleum gases, the composition of such samples being determined by analysis.

(2) Pure or very nearly pure paraffin hydrocarbons, the composition of which was checked by analysis.

(3) Synthetic samples of known composition made by mixing known weights of pure compounds.

(4) Synthetic mixtures of air and hydrocarbons made by mixing a known volume of air with one of the samples contained in the three previous types.

The compositions of the several samples tested are noted in the tables. Analysis of the samples was by low-temperature fractionation, which is accurate to about ±0.3 per cent. The compositions of the synthetic samples are approximately of the same degree of accuracy.

Comparison of Experimental and Calculated Dew Points. The values tabulated below are those determined by the writer over a period of about three and one-half years at various times when certain specific data were required. The apparatus used for all the determinations was essentially that described previously, the only real differences in the various apparatus used being in dimensions and arrangement. The accuracy with which the compositions of the several samples are expressed has been covered. The temperature values are probably accurate to ±1° F. (±0.6° C.) in most cases except when below −30° F. (−34° C.). Experimental dew-point values expressed to 0.1° F., which are not followed by footnote reference, indicate that the thermometer used in these instances was read that closely and was probably correct to within ±0.2° F. (0.1° C.). Values designated by the footnote indicate that the thermometer used in such instances was graduated to 1.0° F., and consequently the fractional parts of a degree had to be estimated. The theoretical dew-points are calculated by use of Raoult's law as demonstrated later in this paper. The accuracy of such calculated values, assuming Raoult's law to be correct, depends on the accuracy of the vapor-pressure tables. The tables used in these calculations are a compilation of what are supposed to be the best data obtainable. The vapor pressures are expressed to three significant figures and are probably about that accurate for normal temperatures. If this is the accuracy of the tables, then the calculated dew points are accurate within about 0.1° F. (0.06° C.) in some ranges and within somewhat less than 0.5° F. (0.3° C.) in others. The reason for this variation in accuracy is the use of three significant figures in the tables, regardless of the size of the number.

Table I gives the dew points found for the first three types of samples. Sample 1 is the only example of the first type. Samples 2, 3, 4, 5, and 6 are of the second type. The remainder of the samples are of the third type. Numbers 7, 8, 9, 10, 11, and 12 were synthesized from samples 2 and 5. Samples 13, 14, and 15 were made from samples 2, 3, and 5.

Table I. Dew Points of Paraffin Hydrocarbons and Commercial Paraffin Hydrocarbon Products

Sample	Composition		Absolute Pressure		Dew Point		
	Gas	Moles			Experimental	Theoretical	
		%	Mm. Hg.	Lbs./sq. in.	° F.	° F.	(° C.)
1	Propane	3.6	1185	22.91	+45.5	+46.2	(+7.9)
	Isobutane	32.4	895	17.31	+32	+32.5	(+0.3)
	n-Butane	63.5	571	11.04	+11	+11.2	(−11.6)
	Isopentane	0.5	383	7.41	− 6	− 5.7	(−21.0)
			154	2.98	−40.7[a]	−39.8	(−39.9)
			89	1.72	−57.5[a]	−57.5	(−49.7)
2	Propane	100.0	762	14.73	−43.5[a]	−43.6	(−42.0)
3	Isobutane	92.5	762	14.73	+12.7[a]	+12.4	(−10.9)
	n-Butane	7.5					
4	Isobutane	100.0	1986	38.40	+60.0	+59.7	(+15.4)
			1666	32.22	+50.0	+50.0	(+10.0)
			1384	26.76	+40.0	+39.9	(+4.4)
			1288	24.91	+36.0	+36.2	(+2.3)
			1190	23.01	+32.1	+32.0	(0.0)
5	Isobutane	2.6	762	14.73	+31.5[a]	+31.2	(−0.5)
	n-Butane	97.4					
6	Isopentane	100.0	624	12.07	+71.8	+72.2	(+22.3)
			392	7.58	+50.0	+50.4	(+10.2)
			265	5.12	+32.4	+33.1	(+0.6)
7	Propane	17.2	762	14.73	+24.5[a]	+24.1	(− 4.4)
	Isobutane	2.1					
	n-Butane	80.7					
8	Propane	33.6	762	14.73	+17	+16.6	(− 8.6)
	Isobutane	1.7					
	n-Butane	64.7					
9	Propane	45.5	762	14.73	+10.7[a]	+10.1	(−12.2)
	Isobutane	1.4					
	n-Butane	53.1					
10	Propane	56.8	762	14.73	+ 3.7[a]	+ 3.4	(−15.9)
	Isobutane	1.1					
	n-Butane	42.1					
11	Propane	71.2	762	14.73	− 6.5[a]	− 7.1	(−21.7)
	Isobutane	0.7					
	n-Butane	28.1					
12	Propane	88.9	762	14.73	−24.7[a]	−25.3	(−31.8)
	Isobutane	0.3					
	n-Butane	10.8					
13	Propane	11.0	762	14.73	+24	+24.2	(− 4.3)
	Isobutane	15.5					
	n-Butane	73.5					
14	Propane	73.5	762	14.73	−11.5[a]	−11.3	(−24.1)
	Isobutane	6.0					
	n-Butane	20.5					
15	Propane	3.1	762	14.73	+19.5[a]	+19.5	(− 6.9)
	Isobutane	56.9					
	n-Butane	40.0					

[a] See paragraph on Comparison of Experimental and Calculated Dew Points.

The samples of the fourth type are presented in Table II. The composition is given in terms of the percentage of air and of one of the previous samples. Reference must be made to Table I for composition of the hydrocarbon mixed with the air. The theoretical dew points are calculated in the same way as those for the previous table, except that the partial pressure of the hydrocarbons is used as their total pressure in the calculations. This partial pressure is found by multiplying the given pressure by the percentage of hydrocarbon sample, and dividing by 100. The air is treated merely as a diluent of the vapor and is supposed to have no effect on the dew.

TABLE II. DEW POINTS OF PARAFFIN HYDROCARBONS AND AIR

SAMPLE	COMPOSITION Gas	COMPOSITION Volume	ABSOLUTE PRESSURE		DEW POINT Experimental	DEW POINT Theoretical	
		%	Mm. Hg	Lbs./sq. in.	° F.	° F.	(° C.)
16	Sample 1	25	3100	59.44	+26	25.5	(− 3.6)
	Air	75	2314	44.75	+12	11.7	(−11.3)
			1308	25.29	−10	−12.5	(−24.7)
			801	15.49	−29	−30.5	(−34.7)
17	Sample 1	20	1369	26.47	−17	−19.2	(−28.4)
	Air	80	564	10.91	−47	−49.2	(−45.1)
18	Sample 1	10	3950	76.38	− 6	− 5.0	(−20.6)
	Air	90	2324	44.94	−23	−25.2	(−31.8)
19	Sample 4 Air	91 9	1525	29.49	+40.0	+40.0	(+ 4.4)
20	Sample 4 Air	80 20	1498	28.97	+32.3	+32.4	(+ 0.2)
21	Sample 4 Air	70 30	1712	33.10	+32.5	+32.4	(+ 0.2)
22	Sample 6 Air	90 10	294	5.69	+32.4	+33.1	(+ 0.6)
23	Sample 6 Air	80 20	335	6.48	+32.6	+33.5	(+ 0.8)
24	Sample 6 Air	70 30	379	7.33	+32.6	+33.2	(+ 0.7)
25	Sample 6 Air	50 50	532	10.29	+32.6	+33.3	(+ 0.7)
26	Sample 6 Air	30 70	888	17.17	+32.4	+33.5	(+ 0.8)

The results of the experimental work may be summarized by the statement that the calculations made with Raoult's law check the determined values to within the limits of experimental accuracy. The values not checking the theoretical dew points either did not depend on Raoult's law (those for pure isopentane) or else were more dependent on other physical laws or assumptions (mixtures of sample 1 and air at lower temperatures).

DERIVATION OF DEW-POINT EQUATIONS

The nomenclature used in the equations appearing in this section is summarized in the following table:

p = partial pressure
M = mole fraction
P = vapor pressure
P_T = total pressure

Subscripts:

A refers to component A
B refers to component B
C refers to component C
P refers to propane
IB refers to isobutane
NB refers to n-butane
IP refers to isopentane
NP refers to n-pentane
L refers to liquid phase
V refers to vapor phase

Raoult's law gives for perfect solutions the equations:

$$p_{AL} = M_{AL}P_A \qquad (1)$$

$$p_{BL} = M_{BL}P_B, \text{ etc.} \qquad (2)$$

The total pressure of the mixture equals the sum of the partial pressures:

$$P_{TL} = M_{AL}P_A + M_{BL}P_B + \ldots. \qquad (3)$$

Solving this equation for M_{AL}:

For two component mixtures,

$$M_{AL} = \frac{P_T - P_B}{P_A - P_B} \qquad (4)$$

For three component mixtures,

$$M_{AL} = \frac{P_T - P_B + M_{CL}(P_B - P_C)}{P_A - P_B} \qquad (5)$$

Similar equations may be written for any number of components. These equations refer to liquid mixtures and are considered to represent the conditions obtained in the very first dew formed. The next step is to substitute vapor composition for liquid composition:

Dalton's law gives the equation:

$$p_{AV} - M_{AV}P_{TV} \qquad (6)$$

Equilibrium between vapor and liquid give:

$$M_{AL}P_A = P_{AL} = p_{AV} = M_{AV}P_T \qquad (7)$$

$$M_{AV} = \frac{M_{AL}P_A}{P_T} \qquad (8)$$

From Equations 4 and 8, for two component mixtures,

$$M_{AV} = \frac{P_A\,(P_T - P_B)}{P_T\,(P_A - P_B)} \qquad (9)$$

For three component mixtures,

$$M_{AV} = \frac{P_A[P_C(P_T - P_B)}{P_T[(P_A - P_B)} + \frac{M_{CV}P_T(P_B - P_C)]}{P_A - P_B]} \qquad (10)$$

For each additional component the equation practically doubles in complexity. It is obvious that this type of equation becomes unmanageable for more than three components. In any event, it is of the indirect type, giving the desired result in vapor pressures rather than temperatures. Moreover, the one equation contains four or more variables, depending on the number of components in the mixture. This means that three of these variables must be assigned values before the equation is solved. The vapor pressures are always assumed since they are interdependent. This leaves either the composition or the total pressure to be fixed.

The complexity of the theoretical dew-point equations makes it desirable to determine some other method for calculating dew points. There is, of course, the cut-and-try method, more often termed the "approximation" method. This method works very well when the dew point is known to within two or three degrees. In this method the temperature is found at which:

$$\frac{M_{AV}}{P_A} + \frac{M_{BV}}{P_B} + \frac{M_{CV}}{P_C} + \ldots.\ \frac{1}{P_T} \qquad (11)$$

This equation is derived from Equation 8 and its analogs.

Another method of determining dew points would be by some general empirical equation in which the constants depended on some known property. A dew-point curve (Figure 3) for a two-component mixture gives no hint as to what form a general equation should take. An empirical equation covering such a curve becomes rather complex if any accuracy is desired.

The graph (Figure 2), representing dew points of a three-component mixture, at once suggests an empirical method of representing the dew points of such mixtures. In Figure 2 the isothermal dew-point lines all originate on one side of the chart, are all straight lines, and are practically parallel. An equation indicating the point of origin of these lines and their slope should represent all conditions in the chart. This equation,

$$X = M_{PV} + 0.456\ M_{IBV} \qquad (12)$$

gives the point, X, at which a dew-point line passing through the composition determined by M_{PV} and M_{IBV} intersects the n-butane to propane side of the chart. This X is in terms of percentage of propane. The constant factor 0.456 is found by determining the composition of a propane and n-butane mixture, which has a dew point equal to the dew point of pure isobutane. The 0.456 is the mole fraction of propane in such a mixture. Thus, the dew points of three-component mixtures may be expressed in terms of the dew points of a two-component mixture and one additional factor which is determined in turn from the same two-component mixture.

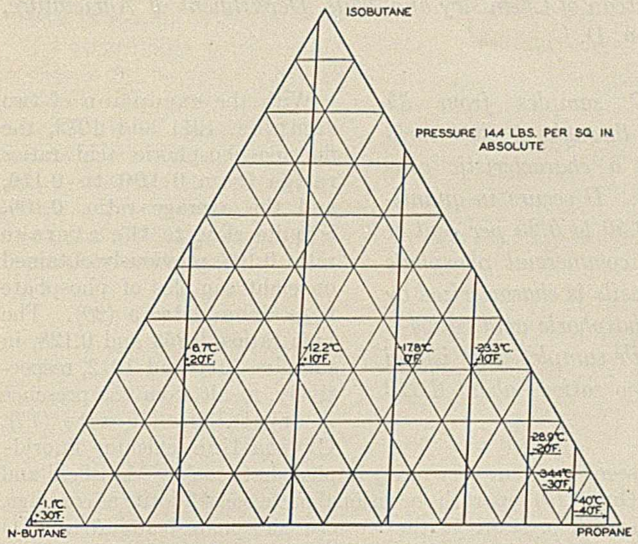

Figure 2. Dew Points of Three-Component Mixture

Since the dew-point lines in Figure 2 are not exactly parallel it is desirable to determine the amount the empirical equation deviates from the theoretical values. The following table gives the maximum deviations found for several selected temperatures:

Dew-Point Temp.	Maximum Deviation of Empirical Values from Theoretical
° F.	° F.
+30	+0.1
+20	+0.1
+10	−0.1
0	+0.3
−10	+0.3
−20	+0.6
−30	+0.3
−40	+0.1

The average deviation for the entire chart is approximately 0.1° F. The empirical equation is nearly as accurate as the original data and is considerably more accurate than necessary for practical purposes.

It is neither easy nor practical to draw a chart representing dew points for more than three-component mixtures, but reasoning by analogy would indicate that the same scheme used for three components could be applied to any number of components. This was done for a five-component mixture containing propane, isobutane, n-butane, isopentane, and n-pentane. The two component system used as a reference is that of propane and n-pentane (see Figure 3). The equation is:

$$X = M_{PV} + 0.905\,M_{IBV} = 0.805\,M_{NBV} + 0.262\,M_{IPB} \quad (13)$$

wherein X is the composition (expressed as percentage of propane) of a mixture of propane and n-pentane having a dew point equal to that of the five-component mixture whose composition is expressed by M_{PV}, M_{IBV}, M_{NBV}, and M_{IPV}. This empirical representation introduces the following maximum deviations:

Dew-Point Temp.	Composition	Max. Deviation
° F.		° F.
+90	$M_{MPV} + M_{IBV}$	−0.3
+60	$M_{NPV} + M_{IBV}$	−1.5
+30	$M_{IPV} + M_{PV}$	+2.0
0	$M_{NBV} + M_{PV}$	+4.5
−30	$M_{IPV} + M_{PV}$	−2.3

At first glance these errors seem rather serious, but further consideration shows that the mixtures having these large errors are unnatural. For instance, there is no possibility of obtaining mixtures of propane and isopentane directly from natural sources. Such a mixture must be synthesized from the pure compounds, and the writer can conceive of no occasion when this would be of any practical use. The largest error occurring in natural two-component mixtures is about 2° F., which is not too large for practical application of the equation. As the number of components in the mixture increases, the error decreases. For instance, a mixture of the following composition:

	%
Propane	40
Isobutane	10
n-Butane	20
Isopentane	15
n-Pentane	15

has a dew point of 46.3° F. by the empirical method while the theoretical dew point is 46.2° F. (The above composition was chosen at random and not because it had almost the same dew point by both methods.)

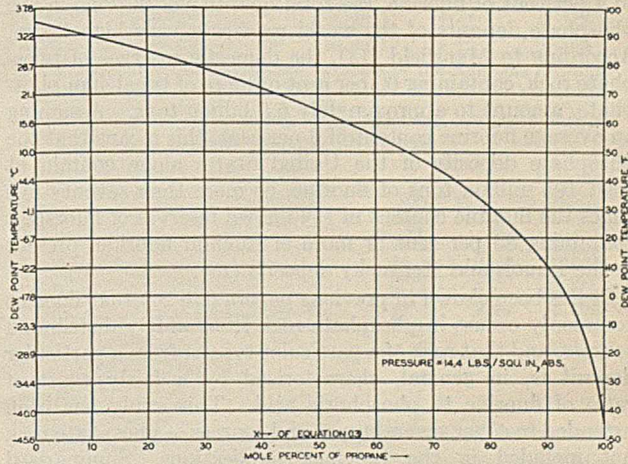

Figure 3. Dew Points of Propane-n-Pentane Mixtures

It must be remembered that the above empirical equations apply at one total pressure only. A corresponding curve and equation must be determined for each different pressure.

Conclusion

Raoult's law gives a surprisingly accurate method for determining dew points of paraffin hydrocarbon mixtures. It can probably be assumed that Raoult's law will be sufficiently accurate for use in calculating all vaporization and condensation phenomena pertaining to paraffin hydrocarbons of any molecular weight, as long as no attempt is made to cover too great a range in volatility.

The empirical method of calculating dew points derived in this report suggests that relatively simple equations and curves could be found to represent any kind of vaporization or condensation phenomena with sufficient degree of accuracy for all practical uses. Such equations and curves would be valuable in that they could be based on a theoretical foundation which is more accurate than usual for theoretical assumptions, and that they could be safely used to predict results with very little experimental support.

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Occurrence of Fluorine in Natural Phosphates

Further Studies

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ANALYSES of 137 samples from 34 localities and countries throughout the world indicate that fluorine is a characteristic constituent of phosphate rock. It occurs in quantities ranging from about 0.40 to 4.25 per cent of the sample. In general, commercial phosphate rock from continental deposits is characterized by relatively high fluorine–phosphoric acid ratios—about 0.090 to 0.140—while samples from island deposits have relatively low ratios—about 0.010 to 0.085.

PHOSPHATE rock is the principal source of fluorine compounds—chiefly barium, magnesium, and sodium fluosilicates—used in the laundry industry, in the manufacture of cement-hardening preparations, and as insecticides. It is also an important source of fluorine compounds for use in the manufacture of iron enamel ware and opalescent glass. The fluorine compounds used for these purposes are obtained principally as by-products of the manufacture of superphosphate.

Although phosphate rock usually contains only about 3 to 4 per cent of fluorine, the total quantity of fluorine in the phosphate deposits of the world reaches a very high figure. According to Mansfield (*14*), the domestic reserves of phosphate rock, containing 60 per cent or more of tricalcium phosphate, amount to approximately 6.5 billion tons. Assuming an average fluorine content of 3 per cent, this means that the phosphate deposits of the United States alone contain at least 195 million tons of fluorine, or more than seventy-five times the fluorine content of the known reserves of fluorspar, containing 85 per cent or more of calcium fluoride, present in the Illinois and Kentucky deposits (*16*).

It has been shown in previous papers (*13*, *20*) that fluorine commonly occurs in phosphate rock from widely distributed sources, and that rock of a particular type or from a particular deposit is, in general, characterized by a fairly constant ratio of fluorine to phosphoric acid. This study has been extended to cover several types and sources of phosphate rock not included in the previous publications. Summarized data on 137 samples from 34 localities and countries throughout the world are given in the present paper.

Phosphoric acid was determined by the official methods (*2*), the gravimetric procedure being used on some samples and the volumetric procedure on others. All fluorine determinations were made by the volatilization method as originally outlined by Wagner and Ross (*27*) and later modified by Reynolds, Ross, and Jacob (*12*, *21*). This method accounts for about 93.5 per cent of the fluorine present in phosphate rock. Consequently, all the figures for fluorine are calculated to 100 per cent recovery on the basis of an actual recovery of 93.5 per cent. All results are calculated to the moisture-free basis (105° to 110° C.).

MONTANA PHOSPHATE ROCK

Extensive phosphate deposits have been discovered in the Elliston (*24*), Garrison and Phillipsburg (*18*), Maxville (*19*), Melrose (*7*, *22*), and the Three Forks-Yellowstone Park (*5*) regions of Montana, but none of these deposits has been worked commercially until quite recently, when development of the Garrison field was started. The percentages of phosphoric acid and fluorine in thirteen prospect samples from this field are given in Table I.

With the exception of two samples, 1011 and 1012, the fluorine–phosphoric acid ratios range from 0.100 to 0.116, and the average ratio, 0.106, is quite close to the average ratio 0.108, previously obtained on eight samples of phosphate rock from Idaho (*20*). The high ratios, 0.253 and 0.128, in samples 1011 and 1012, respectively, result from the presence of crystalline fluorite (*10*). Crystalline calcium fluoride seems to occur very rarely in phosphate rock. Mansfield and Girty (*15*) report the occasional presence of fluorite as coatings, seams, or stains in the western phosphates, and Artini (*1*) found small quantities of fluorite in crystalline phosphate rock from Palestine.

Table I. Phosphate Rock from Garrison, Mont.

Sample	P_2O_5	Fluorine	Fluorine : P_2O_5 Ratio
	%	%	
1011	27.67	6.99	0.253
1013	28.85	2.91	0.101
1018	29.81	2.99	0.100
1016	30.27	3.05	0.101
1009	31.39	3.19	0.102
1019	31.47	3.66	0.116
1020	32.24	3.39	0.105
1007	32.54	3.54	0.109
1017	34.92	3.80	0.109
1014	35.12	3.80	0.108
1012	36.07	4.60	0.128
1008	36.96	4.05	0.110
1010	37.47	3.83	0.102
Av.[a]	32.82	3.47	0.106

[a] Excluding samples 1011 and 1012.

Table II. Tennessee Phosphatic Limestone

Sample	Location of Deposit	P_2O_5	Fluorine	CO_2	Fluorine: P_2O_5 Ratio
		%	%	%	
775	Unknown	10.09	1.24	28.91	0.123
446	Gordonsburg[a]	10.16	1.03	23.19	0.101
579	Mountpleasant[b]	10.53	1.20	30.12	0.114
445	Wales[b]	10.61	1.13	28.80	0.107
916	Mountpleasant[b]	11.22	1.12	28.22	0.100
444	Mountpleasant[b]	11.38	1.57	28.31	0.138
917	Gordonsburg[a]	11.68	1.05	25.57	0.090
447	Mountpleasant[b]	14.04	1.56	26.22	0.111
791	Unknown	15.45	1.68	18.88	0.109
770	Unknown	19.13	2.28	14.86	0.119
	Av.	12.43	1.39	25.31	0.111

[a] Leipers formation.
[b] Bigby formation.

TENNESSEE PHOSPHATIC LIMESTONE

Phosphatic limestones occur in close association with the brown- and blue-rock phosphate deposits of Tennessee (*25*). In fact, these phosphate-rock deposits are generally conceded to have been formed, for the greater part, by the leaching of phosphatic limestones by carbonated waters. In the brown-rock deposits of Mountpleasant and Wales, the phosphatic limestone belongs to the Bigby formation, and it usually occurs in the form of bowlders or "horses." In the blue-rock deposits of Gordonsburg, the phosphatic limestone belongs to the Leipers formation, and in some places it directly underlies the phosphate deposits. Although considerable quantities of phosphatic limestone occur in Tennessee, the greater portion of it contains a relatively low percentage of phosphoric acid, and very few attempts have been made to utilize it commercially. Within recent years, a comparatively small tonnage has been marketed as a mineral supplement for the feeding of poultry and livestock.

The percentages of phosphoric acid, fluorine, and carbon dioxide in ten samples of phosphatic limestone are given in Table II. As would be expected, the composition of this material varies considerably with different samples. The fluorine–phosphoric acid ratios range from 0.090 to 0.138 with an average of 0.111, which is very close to the average ratios, 0.111 and 0.117, previously found (*20*) in fifteen samples of brown-rock and six samples of blue-rock phosphate, respectively.

TENNESSEE WHITE AND KIDNEY PHOSPHATES

The white-rock phosphate deposits of Tennessee (*6*, *9*, *25*) occur principally in Perry and Decatur counties, and to a less extent in Maury County. The phosphate occurs principally in pockets which in some cases contain very high-grade material. Owing to the uncertain character of the deposits and their remoteness from railway lines, they have not been worked to any considerable extent, but recent reports indicate a revival of interest in their commercial possibilities.

The kidney or black nodular phosphates (*8*) occur as inclusions in the blue-rock phosphate and also as relatively small individual deposits in the Chattanooga shale. They are not of commercial interest at present.

TABLE III. PHOSPHATE ROCK FROM MISCELLANEOUS DEPOSITS IN THE UNITED STATES

SAMPLE	LOCATION OF DEPOSIT	P_2O_5 %	FLUORINE %	FLUORINE: P_2O_5 RATIO
	TENNESSEE KIDNEY PHOSPHATE			
1049[a]	Boma, Putnam County	31.22	3.09	0.099
	TENNESSEE WHITE-ROCK PHOSPHATE			
1031	Godwin, Maury County	35.80	3.80	0.106
1048	Tom's Creek, Perry County	30.20	3.06	0.101
	SOUTH CAROLINA PHOSPHATE			
495[b]	Unknown	16.07	2.20	0.137
650[b]	Unknown	28.86	3.43	0.119
1138[c]	Unknown	27.85	3.77	0.135
1139[c]	Johns Island	26.92	3.58	0.133

[a] Sample from cut on Tennessee Central Railroad.
[b] Museum sample.
[c] Commercial material.

The percentages of phosphoric acid and fluorine in two samples of white-rock and one sample of kidney phosphate are given in Table III. The figures indicate that the fluorine–phosphoric acid ratios in these types of phosphate are slightly lower than those in brown- and blue-rock phosphate and phosphatic limestone.

SOUTH CAROLINA PHOSPHATE

The South Carolina phosphates (*23*, *26*) were the first deposits of phosphate rock discovered in the United States, and for approximately fifty years they furnished important quantities of phosphate rock for the domestic and export trades. Exploitation of these deposits ceased, however, several years ago, owing to the low grade of the rock and the cost of mining in competition with Florida land-pebble phosphate. It is estimated (*14*) that these deposits still contain about 9 million tons of phosphate rock.

Analyses of four samples of South Carolina phosphate (Table III) show fluorine–phosphoric acid ratios ranging from 0.119 to 0.137, with an average of 0.131. It is interesting to note that in proportion to the phosphoric acid content, South Carolina phosphate contains, in general, more fluorine than any of the other domestic types of phosphate rock.

FOREIGN PHOSPHATES

The figures given in Table IV show that the North African phosphates are characterized by very high fluorine–phosphoric acid ratios, the values for fourteen samples ranging from 0.119 to 0.143 with an average of 0.129. In this respect, the North African phosphates are similar to South Carolina phosphate. All the samples were taken from shipments of commercial material.

TABLE IV. PHOSPHATE ROCK FROM NORTH AFRICA

SAMPLE	LOCATION OF DEPOSIT	P_2O_5 %	FLUORINE %	FLUORINE: P_2O_5 RATIO
	ALGERIA			
560	Dyr	23.39	3.35	0.143
551	Tebessa	26.10	3.43	0.131
558	Rebiba	26.84	3.65	0.136
562	M'Zaita	28.59	3.68	0.129
557	Tocqueville	29.38	3.71	0.126
559	Bordj-Redir	32.34	4.16	0.129
	EGYPT			
555	Kosseir	30.60	3.65	0.119
	MOROCCO			
453	Unknown[a]	33.47	4.15	0.124
563	Unknown[a]	34.30	4.28	0.125
1162	Unknown[a]	35.19	4.25	0.121
	TUNIS			
552	Gafsa	26.72	3.46	0.129
553	Gafsa	29.13	3.77	0.129
556	Kalaa-Djerda	26.91	3.48	0.129
561	M'Dilla	28.66	3.72	0.130

[a] This sample is from either the Boujniba or the Kourigha deposits.

TABLE V. PHOSPHATE ROCK FROM MISCELLANEOUS FOREIGN CONTINENTAL DEPOSITS

SAMPLE	LOCATION OF DEPOSIT	P_2O_5 %	FLUORINE %	FLUORINE: P_2O_5 RATIO
582	British Columbia[a]	24.11	2.64	0.109
1154[b]	Tallinn, Esthonia	16.78	1.49	0.089
1155[c]	Tallinn, Esthonia	25.68	2.44	0.095
1156[c]	Tallinn, Esthonia	26.48	2.38	0.090
1157	Kapunda, South Australia	30.18	3.62	0.120
1158	Port Clinton, South Australia	33.53	3.32	0.099

[a] Crow's Nest Pass area.
[b] Run-of-mine material.
[c] Commercial material.

TABLE VI. PHOSPHATE ROCK FROM ISLAND DEPOSITS

SAMPLE	P_2O_5 %	FLUORINE %	FLUORINE: P_2O_5 RATIO
ANGAUR ISLAND (PELEW GROUP)			
1223	40.00	2.96	0.0740
CHRISTMAS ISLAND (MALAY ARCHIPELAGO)			
452	39.46	1.32	0.0334
CURAÇAO ISLAND (DUTCH WEST INDIES)			
943	40.66	0.38	0.0094
984	38.71	0.75	0.0194
985	38.59	0.70	0.0181
1022	37.89	0.91	0.0242
JUAN DE NOVA ISLAND (SEYCHELLES GROUP)			
1222	32.29	1.68	0.0520
MAKATEA ISLAND (SOCIETY GROUP)			
1159	38.22	3.25	0.0850
NAURU ISLAND (PACIFIC OCEAN)			
450	38.92	2.62	0.0673
1160	39.21	2.10	0.0536
OCEAN ISLAND (GILBERT GROUP)			
451	40.32	2.97	0.0736
1161	40.87	3.29	0.0805

The percentages of phosphoric acid and fluorine in samples of phosphate rock from the Crow's Nest Pass area, British Columbia; Tallinn, Esthonia; and Kapunda and Port Clinton, South Australia, are given in Table V. The fluorine–phosphoric acid ratio, 0.109, in the British Columbia rock is very close to the average ratios found in samples of Idaho and Montana phosphate (Table VII). This is probably to be

Table VII. Summary of Fluorine–Phosphoric Acid Ratios in Natural Calcium Phosphate

Type or Source of Phosphate	Samples Analyzed	P_2O_5		Fluorine		Fluorine:P_2O_5 Ratio	
		Range	Av.	Range	Av.	Range	Av.
		%	%	%	%		
UNITED STATES							
Florida hard rock[a]	9	31.25–35.86	34.59	3.35–3.95	3.75	0.104–0.112	0.108
Florida land pebble[a]	22	30.52–35.96	32.89	3.86–4.08	3.94	0.109–0.130	0.120
Florida soft[a,b]	4	25.47–34.94	30.42	1.23–3.79	2.57	0.042–0.108	0.084
Florida waste pond[a,b]	9	18.18–25.31	22.41	1.04–2.02	1.49	0.0571–0.0798	0.0665
Idaho[a]	8	30.15–34.96	32.37	3.34–3.70	3.48	0.105–0.111	0.108
Montana (Garrison)	11	28.85–37.47	32.82	2.91–4.05	3.47	0.100–0.116	0.106
South Carolina	4	16.07–28.86	24.93	2.20–3.77	3.25	0.119–0.137	0.131
Tennessee blue rock[a]	6	27.90–33.65	30.74	3.29–3.95	3.58	0.115–0.119	0.117
Tennessee brown rock[a]	15	29.40–37.51	32.83	3.22–4.08	3.66	0.106–0.116	0.111
Tennessee kidney	1	....	31.22	....	3.09	....	0.099
Tennessee phosphatic limestone	10	10.09–19.13	12.43	1.03–2.28	1.39	0.090–0.138	0.111
Tennessee white rock	2	30.20–35.80	33.00	3.06–3.80	3.43	0.101–0.106	0.104
Wyoming (Cokeville)[a]	4	26.60–29.79	28.75	3.10–3.51	3.36	0.116–0.118	0.117
NORTH AFRICA							
Algeria	6	23.39–32.34	27.77	3.35–4.16	3.66	0.126–0.143	0.132
Egypt	1	....	30.60	....	3.65	....	0.119
Morocco	3	33.47–35.19	34.32	4.15–4.28	4.23	0.121–0.125	0.123
Tunis	4	26.72–29.13	27.86	3.46–3.77	3.61	0.129–0.130	0.129
OTHER CONTINENTAL DEPOSITS							
British Columbia	1	....	24.11	....	2.64	....	0.109
Esthonia	3	16.78–26.48	22.98	1.49–2.44	2.10	0.089–0.095	0.091
South Australia	2	30.18–33.53	31.85	3.32–3.62	3.47	0.099–0.120	0.109
ISLAND DEPOSITS							
Angaur (Pelew Group)	1	....	40.00	....	2.96	....	0.0740
Christmas (Malay Archipelago)	1	....	39.46	....	1.32	....	0.0334
Curaçao (Dutch West Indies)	4	37.89–40.66	38.96	0.38–0.91	0.69	0.0094–0.0242	0.0178
Juan de Nova (Seychelles Group)	1	....	32.29	....	1.68	....	0.0520
Makatea (Society Group)	1	....	38.22	....	3.25	....	0.0850
Nauru (Pacific Ocean)	2	38.92–39.21	39.07	2.10–2.62	2.36	0.0536–0.0673	0.0605
Ocean (Gilbert Group)	2	40.32–40.87	40.60	2.97–3.29	3.13	0.0736–0.0805	0.0771
CRYSTALLINE FLUORAPATITE							
Deposits in Canada, Mexico, and New York[a]	6	38.58–40.86	39.84	3.26–4.24	3.76	0.0809–0.1099	0.0945[c]

[a] See reference (*20*).

[b] See reference (*11*).

[c] Theoretical ratio for $Ca_{10}F_2(PO_4)_6$ = 0.0891.

expected, since all these deposits are located in the same general geological formation. The fluorine–phosphoric acid ratios, 0.089 to 0.095, in the Esthonian phosphates are somewhat lower than those generally found in phosphate rock from continental deposits on the western hemisphere. The samples of Esthonian phosphate consisted largely of phosphatized shells from a deposit in the Obolus sandstone region (*17*).

Analyses of twelve samples of phosphate rock from seven widely separated islands (Table VI) show that, in comparison with the majority of the continental phosphates, the island phosphates are characterized by low fluorine–phosphoric acid ratios, 0.0094 to 0.0850. The ratios in the four samples of Curaçao, Dutch West Indies, rock are particularly low, ranging from 0.0094 to 0.0242, with an average of 0.0178.

The summary of results (Table VII) obtained on 137 samples from 34 localities and countries throughout the world indicates that, with very few exceptions, the fluorine–phosphoric acid ratios in phosphate rock from continental deposits are considerably higher than the ratio, 0.0891, theoretically required for fluorapatite, $Ca_{10}F_2(PO_4)_6$. As a matter of fact, crystalline fluorapatite frequently contains more fluorine than corresponds to the theoretical ratio. Analysis of six samples from deposits in Canada, Mexico, and New York gave ratios ranging from 0.0809 to 0.1099 with an average of 0.0945.

Nature and Source of Fluorine Compounds in Phosphate Rock

As previously mentioned, crystalline calcium fluoride seems to occur very rarely in phosphate rock. Microscopical and x-ray investigations (*10*) indicate that, in general, the fluorine in phosphate rock is present principally as a complex calcium fluorphosphate which has the same chemical structure as crystalline fluorapatite. Carnot (*3*, *4*) has advanced the theory that the fluorphosphate is formed by the action of fluorine compounds dissolved in water (particularly sea water) on the calcium phosphates. This theory is the most logical one that has been advanced to account for the high fluorine content of phosphate rock, and experimental confirmation of it is anticipated as the result of studies that are being made in this laboratory. The island phosphate deposits are of comparatively recent origin, and the rock seems to have been exposed to fluorine-bearing waters for an insufficient time to attain the maximum fluorine content.

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Distillation

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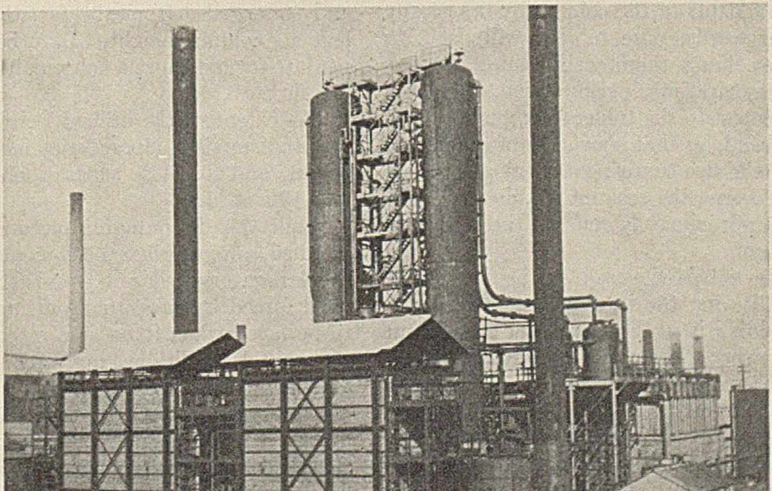
CHEMICAL industry has taken over from the chemical laboratory a number of mechanical operations, such as extraction, evaporation, filtration, drying, and the like. Industry has modified the technic of these adopted operations to meet its own requirements, but in all fundamental characteristics they remain unchanged. The laboratory methods of manipulation are generally inefficient from the points of view of energetics and of time, but in the achievement of the specific purpose of the operation they are usually far more effective than the modified methods of the plant. Thus, it is rare indeed to find in industry a technic of extraction which can compete in effectiveness with the Soxhlet tube in removing the last traces of solute from an insoluble solid, but it is equally rare to find an operation so wasteful of both heat and time. There is, however, one outstanding exception to the rule—namely, distillation. Distillation was adopted by industry from the laboratory, but industry has modified it so that it is not only efficient from the point of view of energetics, but it serves as a method of separation of materials far more successful than any similar technic the laboratory has ever been able to develop. Why the difference?



Courtesy of Standard Oil Co. of Indiana

Pipe Stills for Running Crude Oil

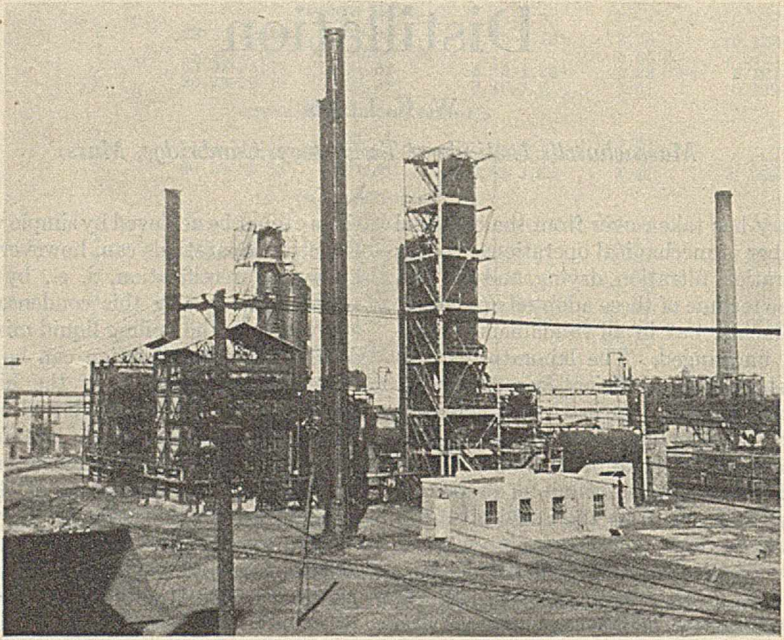
Problem of Laboratory Distillation

Distillation is the separation by vaporization of a liquid mixture of volatile components. Where only one of the components can be volatilized, the operation is called "evaporation" and presents no serious problem. The difficulties inherent in distillation are due to the fact that two or more of the components volatilize simultaneously, even though in different degree. Obviously, therefore, clean-cut separations cannot be achieved by simple vaporization of the mixture. Effective separations can, however, be secured by the process known as rectification, i. e., by condensing a part of the vapor and allowing this condensate to interact with vapor evolved from the boiling liquid mixture at a later stage in the distillation. Rectification can be looked upon as a process of selective absorption of the high-boiling constituents in the vapor by means of a liquid absorbent consisting of the low-boiling components in the form of condensate. This low-boiling constituent is reëvaporated, partly as the result of the heat of condensation of the high-boiling vapor condensed into it and partly by reëvaporation in the still. In order to be effective, contacts between condensate and vapor must be intimate and countercurrent. This contact between phases is secured by the use of a column, up which the vapor rises and down which the condensate flows, designed to give maximum interfacial surface and effective countercurrent action.

While, when properly utilized, rectification is an extraordinarily efficient means of separating volatile constituents, it suffers certain limitations which are extremely serious under laboratory conditions. Because it requires countercurrent contact of vapor and condensate, one must provide a column, or equivalent device, through which flow both liquid and vapor in quantities sufficient to offer a large interfacial surface. Furthermore, in this column one must have a progressive concentration gradient, extending over a considerable length of path. To meet these requirements, the column must contain a considerable amount of liquid, the so-called liquid holdup, and furthermore this liquid must of necessity be a mixture of the components undergoing separation. This mixture in the column itself cannot, in the last analysis, be effectively separated, and this fact constitutes the problem of laboratory distillation.

BENZENE AND TOLUENE MIXTURE

To make clear the point, one may consider, for example, the separation of a mixture of benzene and toluene by means of an adequate column still. When distillation starts, a mixture of benzene and toluene vapors rises from the still. However, in the top of the column this is condensed almost wholly, thereby washing the toluene from the column back to the still and allowing only substantially pure benzene to pass overhead from the top of the column to the condenser. If one continues the distillation, a time is reached at which practically all the benzene has been volatilized out of the still itself, so that only pure toluene remains behind. When this point is first reached, practically pure benzene may still be going overhead. One has now, however, a concentration gradient through the column from pure benzene at the top to pure toluene at the bottom. As distillation is continued beyond this point, driving benzene overhead, it is clear that this benzene must come from the column and must be replaced in the bottom of the column by practically pure toluene. In other words, pure toluene will begin to penetrate further up the column, thereby shortening its effective length as a vapor-separating device. Soon, therefore, the column will fail to separate the toluene completely from the benzene going overhead, so that sharpness of separation is lost, and a mixture of the two components begins to collect in the receiver. Furthermore, the amount of this mixed distillate will obviously be approximately equal to the volume of liquid holdup in the column.



Courtesy of Standard Oil Co. of Indiana

CROSS CRACKING STILLS

In industrial work one solves the problem in the case of batch operations by collecting the intermediate mixed distillate separately and adding it to the charge for subsequent operations. However, where practicable, industry much prefers to operate its stills continuously, thus maintaining in the column a constant amount of holdup of constant composition, which, however, does not interfere in any way with the purity of either distillate or residue, both of which are withdrawn from the equipment at constant rate. It is clear that neither of these methods is convenient for laboratory work.

LABORATORY METHODS

The laboratory has been able to develop no device which can effectively replace the rectification column. However, it has attempted to lessen the ill effects of liquid holdup by reducing its amount. It is obvious that the first method is to reduce the height of the column. However, the interaction of liquid and vapor must be effectively countercurrent, and, if column height is to be lessened, the reduction must be compensated for, either by great increase in the amount of surface of contact per unit height or else by increase in reflux. The most efficient type of column, from the point of view of effectiveness of contact and certainty of countercurrent action, is the bubble cap plate, but for laboratory work its use is almost excluded because of the large amount of liquid that must be carried on the plates. So-called packed columns are more satisfactory. It has long been recognized that the finer the packing the better are the results. However, if packing is made too small, the column floods; i. e., the liquid refuses to flow downward through the column against the rising stream of vapor. Nonetheless, it has been possible to develop columns of moderate liquid holdup and of relatively high efficiency.

The second method of attack is to reduce the cross section of the column in comparison with the size of the still. This, however, slows up distillation rate and makes the time required inordinate. The third method is to increase the amount of reflux. This is indeed effective, but it, too, slows up net distillation rate and suffers also from the fact that it is not entirely equivalent to column height. In other words, one cannot compensate for too short a column, however effective, by increase of reflux.

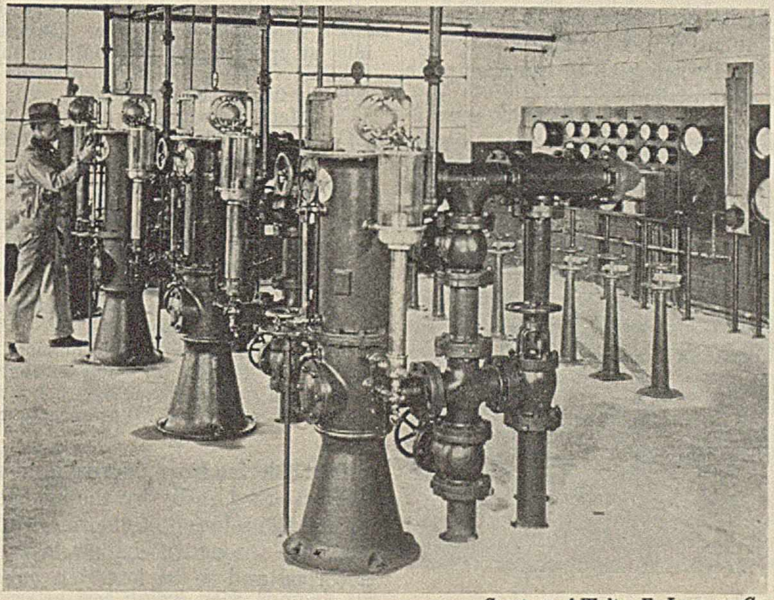
The extent of the difficulties can be appreciated from the fact that modern laboratories have tried columns 35 feet in height, and for close separations recommend columns from 3 to 10 feet high.

While this discouraging picture of the problem is not unjustified, progress has been made in solving it. However, the laboratory did not even attack the problem seriously until forced by pressure from industry. The situation had to be faced when it became essential to separate, under experimental conditions, mixtures whose components differed to a significant degree in no respect save volatility. This necessity was encountered first in the natural gasoline industry. Workers in a number of laboratories contributed to the development of satisfactory apparatus and technic. The result achieved is perhaps best illustrated by the apparatus of Podbielniak (*1*). He uses a tall column, designed to give effective liquid-vapor contact with a minimum of liquid holdup and employs heavy reflux. His apparatus is intended for the separation of relatively low-boiling constituents, but can be modified for higher-boiling components.

IMPORTANCE OF DISTILLATION IN THE LABORATORY

Distillation is needed in the laboratory for two distinct purposes—the analysis of mixtures and the separation of pure components from them. For analytical purposes it has been demonstrated that it is not necessary to employ the high degree of rectification necessary where purity of product is essential. A rectifying column which gives rather poor separation of components from the point of view of purity, will still show sharply the break points in the distillation curve, corresponding to the transition from one component to another. This is due to a counterbalancing of errors, the amount of high-boiling constituent taken overhead with the low being approximately equal to the amount of low boiling left in the high. The more difficult problem is that of purification, especially where total quantities available are small.

While the laboratory technic of distillation has improved greatly in the last decade, much remains to be done. There are three promising lines of attack. In the first place, the laboratory column should be thermally insulated or heat-jacketed. In the second place, more dependable methods of testing the purity of the distillate being collected at any instant should be developed, and finally, the potentialities of vacuum distillation exploited.



Courtesy of Walter E. Lummus Co.

OPERATING FLOOR OF CONTROL HOUSE IN PETROLEUM REFINING UNIT

A rectifying column may be looked upon as a heat engine in which heat is supplied to the still at high temperature, and the waste heat discarded at the top at a lower temperature level. Ideally no heat should be supplied or allowed to escape at any intermediate temperature level. In practice, heat usually dissipates along the column. Where this is not excessive, preventing its loss is perhaps more trouble than it is worth. However, the moment the column must be operated at temperatures either very high or very low, thermal insulation of the column becomes imperative, since otherwise its operation will be completely upset. It is due to this fact that the use of laboratory columns is so often limited to the separation of materials boiling in the neighborhood of room temperature. While the evil can be reduced by insulation, thermal jacketing (preferably with a gas at substantially the same temperature as that of the column) is usually easier and far more effective. It is important to develop a satisfactory laboratory technic for this purpose.

From time immemorial the purity of the distillate coming over at a given instant has been tested by the measurement of vapor temperature. This measurement is subject to serious errors, of which the most important are conduction and radiation losses from the thermometer. It seems probable that other physical methods of testing the purity of distillate, such, for example, as the measurement of refractive index and the like, should prove superior.

HIGH-VACUUM DISTILLATION

One of the most promising lines of attack is the use of high vacuum. Usually, the lower the temperature the greater the volatility differences between materials, and, hence, the easier the separation by distillation, but laboratory workers have not taken advantage of this fact to the extent they should. Since the drop in temperature can be secured only by drop in pressure, and since large pressure decreases are necessary to produce marked changes in temperature, it is probable that vacuum has not been used more widely because workers have tried moderate vacuum and found little advantage. However, with the development of modern high-vacuum technic, it is possible to achieve results hitherto undreamed. It will be necessary, it is true, to use rectification under vacuum, and this always presents difficulties. Thus, it will be imperative to develop extremely effective methods of maintaining constancy of pressure. It is obvious that pressure variation will upset distillation conditions, but it is sometimes not appreciated that the upset is approximately proportional to the percentage variation in pressure and in no sense to the pressure difference. Consequently, a pressure variation, which at atmospheric pressure would have no appreciable effect, can ruin the separation under high vacuum. Furthermore, because the vapor-handling capacity of a column goes down under vacuum, the difficulties due to heat losses from the column increase, and the necessity of effective thermal jacketing becomes greater. Finally, at high vacuum the errors in measuring vapor temperatures increase rapidly so that it becomes much more essential to have improved methods of testing distillate quality. However, despite these problems, the advantages inherent in high-vacuum distillation are so marked that it offers great promise as a laboratory development, both as a method of analysis and for the purification of materials.

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Chlorination of Sewage

C. K. Calvert, *Indianapolis Sanitation Plant, Indianapolis, Ind.*

THE sewage of Indianapolis, with the exception of approximately 3 M. G. D., is delivered to the sewage plant for treatment. The quantity so delivered averages 46.8 M. G. D.

All sewage which reaches the sewage-treatment plant is clarified by a combination of concentrating screens and sedimentation. During the summer months the activated-sludge plant is operated at its greatest capacity, which results in the treatment of about 70 per cent of the sewage flow. The remainder of the sewage goes to the river with no other treatment than clarification.

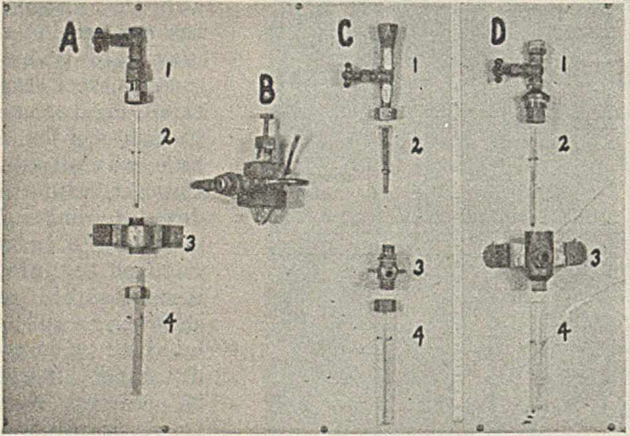

Figure 1. Chlorine Delivery Devices

Prior to the summer of 1930 a number of observations had been made elsewhere on the effect of chlorine on the B. O. D. of sewage. From these various pieces of work it appeared that the chlorination of clarified sewage at Indianapolis might result in improved river conditions.

Laboratory experiments, carried on at Indianapolis during 1929 and again early in 1930, indicated that a reduction of 5-day B. O. D. might be expected, amounting to perhaps 35 per cent of the total, and, on the basis of 10-day incubation, a reduction of 15 to 20 per cent. In these experiments chlorine was applied to give at least a trace of residual after 10 minutes, the quantity being varied throughout the day on the basis of the strength of sewage as indicated by the chlorine demand.

On the basis of the published results and the laboratory experiments made at Indianapolis, the use of chlorine during the summer of 1930 was determined with the hope that river conditions might be improved until such time as extension of the activated-sludge plant could be realized.

In order to simplify the installation—avoiding the use of evaporators and automatic gaseous chlorine machines—an effort was made to apply liquid chlorine so that the quantity of chemical used might be increased to any desired point without material modification of the installation.

A number of devices were tried experimentally, and finally two types of chlorine jets were developed. Both types require constant attention to maintain a uniform application of chlorine, but do not require expert operators. The stoppage of lines and jets, or orifices, by a gummy substance in the liquid chlorine offers some difficulty, but it is believed that this can be overcome by the use of rather large-area filters near the chlorine cylinders.

Liquid-Chlorine Delivery Devices

Figure 1 is a photograph of four chlorine delivery devices which have been taken apart; the pieces are placed one above the other in assembly order, so that each one slips down into the one below to reach an operating position.

A. Glass jet with double outside packing nuts.
B. Variable-orifice device. Chlorine control at top, chlorine inlet at upper right, water inlet at middle front, and water and chlorine delivery point at extreme bottom. A 2-inch glass cylinder fits on the lower part.
C. Metal jet with lead gasket joints.
D. Glass jet with single inside packing nut.
1. Chlorine control head with chlorine entering at top, controlled by needle valve and delivered to jet below.
2. Chlorine delivery jet.
3. Water head with chlorine entering through jet above, and water entering through side opening.
4. Gage glass held to water head with packing nut. The water flows down through this glass and out into a hose clamped on the bottom. The chlorine is delivered from the jet into the upper part of the glass.

Applying chlorine in this fashion results in its reaching the sewage as: (1) ice, (2) water solution, and (3) gas; the relative amount of each depends on: (1) rate of mixture with, (2) the volume of water, and (3) temperature.

The chlorine from chlorine ice is liberated relatively slowly and absorbed easily by the sewage. It is a simple matter to mix the solution of chlorine with the sewage, but the gas may rise through a shallow layer of sewage without being absorbed and so be lost. In one installation the mixture of solution, ice, and gas was delivered below filtros tile, under which the ice and solution passed, and through which the gas escaped in fine bubbles into the sewage. Very little loss of chlorine occurred judging from the odor in the sewer below the point at which application was made.

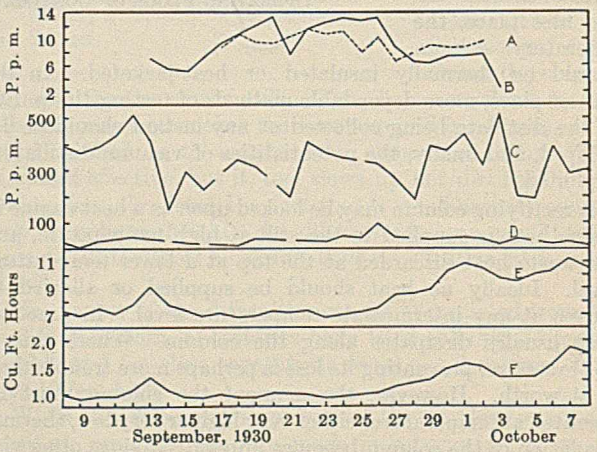

Figure 2. Results of Plant Operation before, during, and after Chlorination

A. Chlorine demand of sewage
B. Chlorine supplied to sewage
C. B. O. D. of sewage
D. B. O. D. of effluent
E. Detention time
F. Air per gallon

Highly chlorinated sewage loses its chlorine if agitated immediately after application, such as falling over a dam or traveling at high velocity over a steep grade. In order to mix the chlorine more thoroughly and intimately with the sewage, a second device was employed:

This device consisted of a 30-inch vitrified tile with the upper end sealed, and the lower end supported about 8 inches from the floor of the sewer. The mixture of chlorine solution, ice, and gas was delivered through a hose under the tile and well toward the top. Another hose line led from the very top of this tile back to the suction side of a Duriron injector. Thus, any gas delivered to the tile was drawn back through the injector, mixed again with water, and delivered to the line as solution. Any gas not absorbed by the water was drawn back through the injector a second time. With this arrangement, chlorine was applied to the sewage with no loss of the gas.

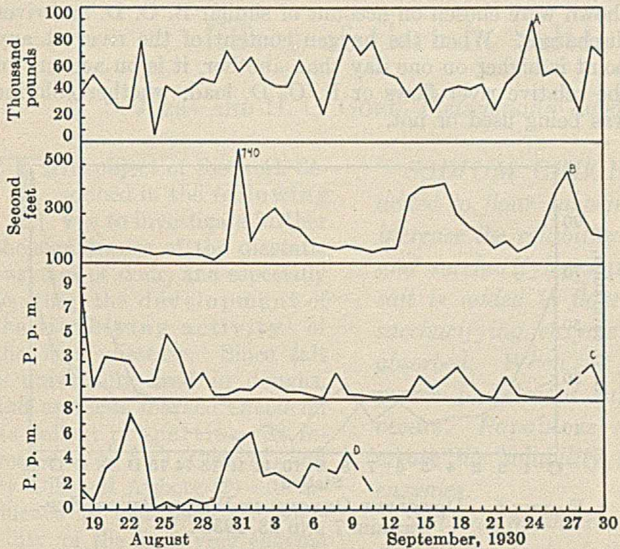

Figure 3. B. O. D. in Combined Plant Effluent and River Condition

A. B. O. D. discharged from plant per day
B. River discharge
C. Minimum dissolved oxygen in river
D. Chlorine in combined plant effluents at outfall (chlorination discontinued September 12, 1930)

Efficiency of Application of Chlorine

It appears from the examination of individual figures that large doses of chlorine may not reduce B. O. D. in the same proportion as small doses. It appears too that chlorine may combine with substances in the sewage to render it inactive to starch-iodide tests and yet reduce the B. O. D. inappreciably.

Any attempt to determine the efficiency of application at Indianapolis is affected by the above conditions. Period averages, when excess chlorine was common, indicate that about 60 per cent of the chlorine applied can be accounted for as free chlorine or satisfied chlorine demand. Actually the whole amount of chlorine used, calculated to parts per million, equals almost exactly the average immediate chlorine demand of the sewage at 9 A. M., 1 P. M., and 4 P. M. However, during much of the time the chlorine demand was materially less than the average, and the application of chlorine was at an excessive rate. It is difficult to arrive at an estimate of the efficiency of application.

Laboratory determinations were made three times daily (during the peak load period) of the B. O. D. and chlorine demand, before and after chlorination. No work was attempted to show what compounds resulted from the reaction between the chlorine and the sewage constituents. Tests were made for free chlorine each hour by the starch-iodide method.

Table I shows the reduction noted in the chlorine demand and 5-day B. O. D. It is seen that the chlorine demand is reduced from seven to ten times as much as the B. O. D. Even though the chlorine demand had been satisfied entirely, the B. O. D. reduction would have been improved but little. This observation is substantiated by the B. O. D. reduction figures on days when free chlorine remained more than 10 minutes.

Table I. Reduction of Immediate Chlorine Demand and 5-Day B. O. D. of Clarified Sewage by Chlorination

(July 26 to September 12, 1930)

	Immediate Demand				5-Day B. O. D.		
Time	Number of determinations	Clarified	Clarified and chlorinated	Reduction	Clarified	Clarified and chlorinated	Reduction
				%			%
9 A.M.	36	5.8	1.7	71	184	166	9.8
1 P.M.	37	9.0	2.9	68	298	275	7.7
4 P.M.	28	9.0	3.0	67	268	249	7.1

Chlorine was applied to the influent to the activated-sludge plant at a point very near that at which the return sludge entered. The concentration of chlorine was held sufficiently low to avoid more than traces coming in contact with the activated sludge, although it was not all combined at this point. Figure 2 shows the results of plant operation before, during, and after chlorination. A glance shows that there was no improvement in operation during the chlorination period. Neither is the increase in detention period and air per gallon in the latter part of September due to chlorination. It is a seasonal change and is anticipated. The color and appearance of the activated sludge seemed to be improved during the chlorination period.

Indianapolis sewage is quite fresh when it arrives at the treatment plant. It is probable that chlorination of septic sewage might result in a much greater reduction in B. O. D. than was noted in this work, and that under such conditions it might improve materially the operation of a biologic-treatment plant.

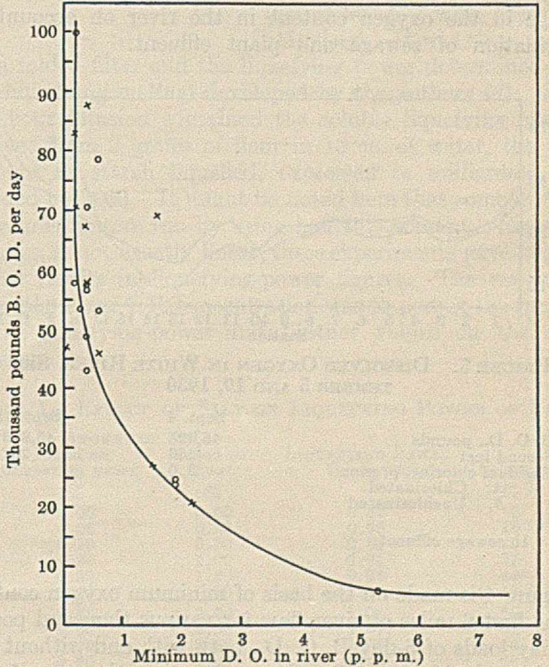

Figure 4. Effect of B. O. D. Load on River Condition in 1930

×. With chlorine O. Without chlorine

Activated-Sludge Plant

Since it was obvious, from an examination of the B. O. D. reduction effected by chlorination of the clarified sewage and from river inspection, that chlorination was not solving the problem, it was determined to chlorinate so heavily that free chlorine would be maintained in the river itself, with the hope that longer contact and greater concentration might improve the river. For this purpose, advantage was taken of the volume of the effluent from the activated-sludge plant, chlorinating it as well as the clarified sewage, both of which enter the river through the same sewage outfall.

Two main factors control river condition—the organic load added and the dilution afforded by the stream. No account is taken, in this discussion, of the distance, time, or reäeration afforded by riffles, since they are practically the same for the chlorinated and unchlorinated periods. The B. O. D. in the combined plant effluent and the river condition are shown in Figure 3. The organic load and dilution are shown as thousand pounds of 20-day B. O. D. discharged from the plant per day, and the river discharge in second feet.

The measure of river condition is taken as the minimum dissolved oxygen within the first 6 miles of river flow, which is the part most affected. In order to determine the effect of chlorine applied to the sewage, the residual chlorine in the entire plant effluent is also shown. An examination of this graph shows that, with a material reduction in the organic load or an increase in the river discharge, there is a resultant increase in the dissolved oxygen. It will be noted that this increase comes a day late on the graph, approximately this time elapsing between the discharge of sewage and the taking of the sample. In one instance the increase in the minimum oxygen occurs following a day on which no chlorine was applied, although there is no connection between the two conditions. There appears to be no material change in the oxygen content in the river on account of chlorination of sewage and plant effluent.

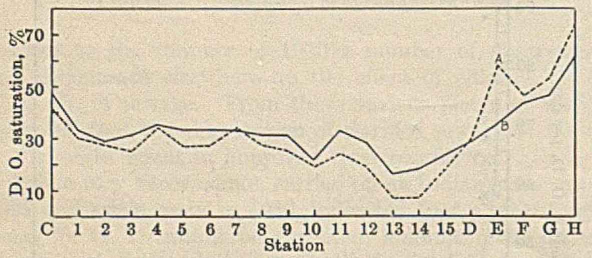

FIGURE 5. DISSOLVED OXYGEN IN WHITE RIVER, SEPTEMBER 5 AND 19, 1930

	Sept. 4	Sept. 18
*B. O. D., pounds	45,927	45,896
Second feet	266	287
*Residual chlorine, p. p. m.	3.0	0

A. Chlorinated
B. Unchlorinated

* In sewage effluent.

Figure 4 is made on the basis of minimum oxygen content in the first 6 miles of river flow for various thousand pound per day loads of 5-day B. O. D., both with and without the addition of chlorine. On the assumption that the 5-day B. O. D. of the clarified sewage may be reduced 10 per cent, it is seen that chlorination can be expected to produce very little improvement in river condition. Assuming, for instance, that the daily load amounts to 50,000 pounds of 5-day B. O. D., and that it may be reduced 10 per cent, or to 45,000 pounds, the improvement in the dissolved oxygen in the river amounts to only 0.12 p. p. m. Assuming again that a reduction of B. O. D. of 25 per cent could be obtained, and the B. O. D. load reduced to 37,500 pounds per day, the improvement in the river amounts to 0.4 p. p. m. of dissolved oxygen. Such a small increase certainly does not warrant the expenditure of much money for chlorine or any other treatment agent.

Figures 5 and 6 show the relation of B. O. D. poundage to river condition between stations 8 and D during days of chlorination and no chlorination. The data for the 4 days shown were chosen on account of similar B. O. D. and river discharges. When the oxygen content of the river at any point is higher on one day than another, it is on account of the relative river flows or B. O. D. load, whether chlorine was being used or not.

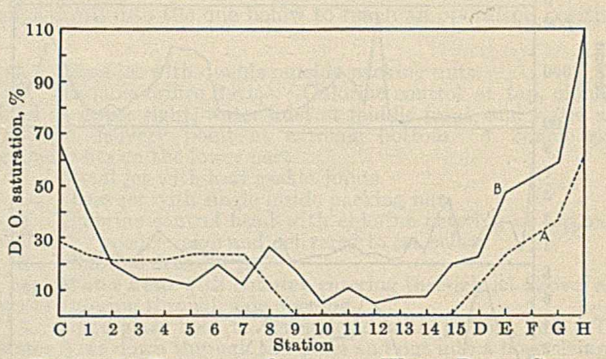

FIGURE 6. DISSOLVED OXYGEN IN WHITE RIVER, SEPTEMBER 7 AND 23, 1930

	Sept. 6	Sept. 22
*B. O. D., pounds	47,218	48,805
Second feet	187	193
*Residual chlorine, p. p. m.	3.8	0

A. Chlorinated
B. Unchlorinated

*In sewage effluent.

There is always danger in drawing general conclusions. The matter presented here is on the basis of the experience gained in using 150,000 pounds of chlorine in one summer.

METHODS

IMMEDIATE CHLORINE DEMAND. In a liter beaker are placed 400 cc. of a 500-cc. sample. Chlorine solution (1 cc. = ±1.0 mg. chlorine), standardized hourly, is run in quickly in not more than 0.5-cc. amounts until free chlorine appears, as shown by the starch-iodide test used as an outside indicator. The remainder of the 500-cc. portion is added, and the titration continued, using smaller portions of chlorine solution at the end.

B. O. D. Standard method. Aged aerated distilled water is used for dilution.

OXYGEN DISSOLVED. Modified Winkler.

CONCLUSIONS

The summer's work leads to the belief that:

1. Chlorine under proper conditions may be applied as a liquid instead of as a gas.
2. The chlorination of Indianapolis sewage reduced the 5-day B. O. D. no more than 10 per cent.
3. Chlorination of clarified sewage resulted in no material improvement in the activated-sludge process.
4. Summer improvement of the White River effected by chlorination can be expected to be negligible with a B. O. D. load of, or greater than, 25,000 pounds per day.

ACKNOWLEDGMENT

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Development of Diastatic Enzymes of Malt and Flour

Effect of Certain Salts, Carbohydrates, and Papain

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SODIUM CHLORIDE or other salts when added to flour suspensions are found greatly to increase the solubility of the diastatic liquefying and saccharifying enzymes of flour. When no salt is added to flour suspensions, part of the saccharifying enzyme is released and then reabsorbed. When salt is present, the full diastatic power is released rapidly, and no absorption occurs. Papain is also found to greatly increase the solubility of both types of diastatic enzymes.

Salt and mash concentrations greatly increase the development of the diastatic liquefying enzymes of malt. Large effects of glucose and maltose in increasing liquefying enzyme development are observed. Papain, too, is effective in increasing the solubility of the liquefying enzyme in malt infusions.

The object of the work described in the following was to investigate further the significance of the diastatic enzymes of flour, and especially to study the development of the liquefying activity[1] of the flour diastase. Since salt is universally used in doughs, and exercises marked effects on its colloid properties—as revealed, e. g., by LeClerc (*7*) and by Dill and Alsberg (*2*)—its influence in increasing the solubility of the liquefying enzyme in flour suspensions has been studied. Proteolytic enzymes also, according to Ford and Guthrie (*4*) and to Stockham (*9*), are present in dough, especially when malt or flour from sprouted wheat is present [see also Collatz (*1*) and Sherwood and Bailey (*8*)]. Work has been also done here on the effect of papain on the release of soluble liquefying enzyme. This work confirms and extends the pioneer work of Ford and Guthrie (*4*).

They found that, in the determination of the activity of the diastase of flours, "the operation is not simply a question of extracting the flour with water and measuring the activity of the extract by allowing it to act on soluble starch in the customary manner."

Ford and Guthrie observed that the duration of the extraction was an important factor. Thus 20 grams of a flour digested with 500 cc. of water for 10 minutes gave a filtrate which showed far more diastatic activity than when the digestion was prolonged for 2 hours. Flours were found to differ greatly in the amounts of diastase which, apparently, become destroyed during the long digestion period. They discovered also that the extent of apparent destruction of diastase varied with the ratio of flour to water. When salts were added to the water in which the flour was steeped, very large increases took place in the diastatic power of the filtrates. Thus potassium chloride present in the water to the extent of 1 per cent increased the diastatic power of the flour filtrate over fourfold. They believed that the effects observed were due to the conservation of the enzyme by the solution of bodies which protected it from destruction.

Papain also was found to augment greatly the solubility of flour diastase. They believed that the papain exercised a dual function. It seemed to liberate a certain amount of the amylase which apparently was present in insoluble form in combination, and at the same time to prevent its destruction. Similar, although on the whole less striking results, were obtained by these authors on barley flour (*3*).

Experiments on Flour

In the first experiment 20 grams of hard flour[2] were mixed with 100 cc. of water containing 0.2 per cent sodium chloride, and beaten thoroughly with a glass rod. Then the mixture was allowed to stand for 1 hour at laboratory temperature (about 20° C.) with occasional stirring. It was then poured on a folded filter and the liquefying power determined with the liquefying method developed by the authors (*6*). Since the flour infusion contained the soluble liquefying enzyme derived from 2 grams of flour in 10 cc. of water, the total amount of starch liquefied, expressed in milligrams, was divided by 2000. It might be noted here that some of these experiments were run by using half this amount. Since the reaction is not exactly linear, these experiments gave slightly higher results in liquefying-power figures. The reason for using the lower 1:10 concentration was to permit the running of the liquefying-power and Lintner values on the same infusions.

Table I. Effect of Salt on Liquefying Power of Flour

Amount of NaCl: Based on digestion water	Based on flour	Liquefying Power Observed	Increase
%	%		%
0.00	0.00	0.66	0
0.05	0.25	0.76	15
0.10	0.50	0.83	25
0.20	1.00	0.91	37
0.30	1.50	0.95	44
0.40	2.00	1.02	53
0.50	2.50	1.06	60
0.60	3.00	1.07	61
0.70	3.50	1.09	64
0.80	4.00	1.11	68
0.90	4.50	1.11	68
1.00	5.00	1.10	66

The amount of sodium chloride used on basis of digestion of water and flour, respectively, and the liquefying powers and their increases are given in Table I.

These results show that a considerable increase of the liquefying power was obtained when sodium chloride was added to the digestion water. The rate of increase reached a

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[1] Fletcher and Westwood [*J. Inst. Brewing*, **36**, 550 (1930)] have recently criticized the method of Józsa and Gore for the determination of liquefying power. The latter intentionally made no theoretical assumptions. Fletcher and Westwood supposed that Józsa and Gore assumed the results were expressed in terms of enzyme and substrate to which a linear relationship could be applied. Their method shows simply the amount of starch actually liquefied by a malt under the explicitly stated conditions. Like most enzyme measurements the activity measured can be applied only under the given conditions.

[2] The hard flour used in this report was a patent flour made from northern spring wheat. The soft flour was a very short patent made from soft winter wheat.

maximum of 60 per cent when 0.5 per cent sodium chloride was used in the digestion water. Above this limit the increase was slow, reaching 66 per cent when 1 per cent of sodium chloride was used.

The liquefying power was not greatly affected when the sodium chloride was added to the filtrate of the solution. Four grams of sodium chloride were added to 100 cc. of the filtrate of a 1.5 flour suspension. The original liquefying power, 0.66, rose to 0.77, corresponding to an increase of 17 per cent.

The diastatic power (degrees Lintner) was also determined by the polarimetric method described by one of the authors (*5*) with different amounts of sodium chloride used in the suspension.

In these experiments 25 grams of flour were mixed with 250 cc. of salt solution. The details were then similar to those mentioned above. The results obtained are shown in Table II.

Table II. Effect of NaCl on Saccharifying Power of Flour

Amount of NaCl: Based on digestion water	Based on flour	Degrees Lintner	Increase
%	%		%
0.0	0.0	49.5	0
0.004	0.04	54.4	9.8
0.01	0.1	54.4	9.8
0.02	0.2	57.6	16.3
0.04	0.4	69.6	40.6
0.10	1.0	82.6	66.8
0.20	2.0	101.6	105.2
0.40	4.0	106.0	114.1
1.00	10.0	114.1	130.5

The diastatic activity when no added salt was present was 49.5° Lintner. When very small amounts of salt were present, even as little as 0.04 per cent of the flour, the Lintner value increased to 54.4°, corresponding to 0.8 per cent. With increasing amounts of salt, the increase of diastatic power of flour filtrate was almost linear until about 2 per cent of salt calculated on the flour, was present. Here the Lintner value was 101.6, an increase of 105.2 per cent. With further increased salt addition (4 and 10 per cent based on flour), the increase in saccharifying activity was less pronounced.

The effect of different salts on the liquefying enzyme was next studied. The experiments were similar to those first described. The concentration in each experiment was 0.5 per cent based on the digestion water and 2.5 per cent based on the flour.

Table III. Effect of Salts on Liquefying Power of Flour

	Liquefying Power	Increase
		%
Check (no salt added)	0.75	..
Potassium hydrogen phosphate (K_2HPO_4)	1.02	35.5
Potassium orthophosphate (K_3PO_4, pH 6.3)	0.96	27.8
Potassium chloride	1.06	41.0
Potassium bromide	1.02	35.1
Potassium iodide (pH 4.4)	0.92	21.8
Potassium chlorate	1.05	39.0
Potassium bromate	1.00	33.1
Potassium iodate (KIO_3, pH 4.3)	0.40	..
Potassium perchlorate	1.06	40.4
Potassium nitrate	1.09	44.3
Potassium sulfate (K_2SO_4)	1.05	39.0
Calcium chloride ($CaCl_2$)	1.03	36.4
Calcium sulfate ($CaSO_4$)	0.95	25.8
Potassium formate	1.00	33.1
Potassium acetate	0.97	29.1
Potassium oxalate	0.93	23.1
Potassium bitartrate (pH 4.3)	0.86	14.5
Potassium cyanide (pH 6.2)	0.93	23.1
Potassium sulfocyanate	1.00	32.4
Potassium ferrocyanide	1.09	44.3
Potassium lactate (pH 4.4)	0.94	24.5

These results show that, except in instances in which the pH of the suspension was appreciably changed by the added salt, increases in liquefying activity ranging from 14.5 to 44.3 per cent occurred.

The lowest pH was found in the case of KIO_3 (pH 4.3). This was in contrast to the highest pH observed in case of K_3PO_4 (pH 6.3). The liquefying powers in these cases were 0.40 and 0.96, respectively. Thus, almost any salt will produce an effect like sodium chloride, provided that the pH is within the optimum range.

Table IV. Effect of Flour-Water Concentration on Liquefying Power

Amt. of Flour	Amt. of Water	Proportion Flour: Water	Liquefying Power	Increase
Grams	*Cc.*			%
200	2000	1:10	1.04	0
400	2000	2:10	1.13	8.6
600	2000	3:10	1.25	20.1
800	2000	4:10	1.27	22.1
1000	2000	5:10	1.33	27.8
200	2000[a]	1:10	1.71	64.4

[a] Plus 10 grams NaCl.

Since sodium chloride and various salts are able to produce a higher enzyme development, it was thought likely that the soluble enzyme content would increase in a flour suspension when the concentration of the flour was increased, owing only to the increasing concentration of the salts present in flour. To test this point, flour suspensions were prepared, using varying amounts of flour and water. The filtrates from these infusions, except the first, were diluted with water so that each sample corresponded to the first sample as to substrate concentration in a given volume of the infusion. The amount of flour and water used, the proportion of water and flour, and liquefying power and its increase are given in Table IV.

These experiments show that not only salt addition but higher flour concentrations increase the liquefying power considerably. Thus in a flour water mixture having the ratio of 1:2, an increase of 27.8 per cent was observed, about half of the optimum increase observed with sodium chloride.

In determining the effect of papain on the liquefying and Lintner values of the flours, a series of 1:10 flour and water suspensions was prepared, containing varying amounts of papain. The suspensions were digested for 2 hours at room temperature.

Table V. Effect of Papain on Liquefying and Saccharifying Power of Flour

Without NaCl

	Hard Flour		Soft Flour	
Papain per 10 Grams Flour	Liquefying power	Degrees Lintner	Liquefying power	Degrees Lintner
Mg.				
0	1.05	44	1.17	33
1	1.20	48	1.19	51
2	1.21	58	1.39	63
5	1.26	72	1.44	82
10	1.31	90	1.55	97
25	1.42	119	1.64	119

With NaCl

		Hard Flour		Soft Flour	
NaCl per 10 Grams Flour	Papain per 10 Grams Flour	Liquefying power	Degrees Lintner	Liquefying power	Degrees Lintner
Mg.	*Mg.*				
200	0	1.65	102	1.76	77
200	1	1.70	103	1.80	79
200	2	1.72	105	1.82	84
200	5	1.77	115	1.90	95
200	10	1.79	120	1.95	109
200	25	1.81	147	2.02	123

The effect of papain was also studied in the case where sodium-chloride was added to the suspension. The liquefying and saccharifying power were determined on the filtrate in the usual manner.

Thus large increases in liquefying power and Lintner values were caused by the papain. When the papain was added to suspensions containing sodium chloride, the rate of increase was less intense.

The rate at which the diastases of flour passed into solution when the flour was mixed with water and continuously stirred was then studied. In case of the liquefying activity, the results were rather irregular, and no satisfactory checks could be obtained.

In the case of the saccharifying enzyme, 200 grams of flour were shaken with 2 liters of water, and poured into a large crystallizing dish. Here the mixture was continuously agitated by a suitably shaped glass rod attached to a low-speed power-driven stirrer. Samples were removed at intervals and filtered on folded filters, and the saccharifying power determined in the filtrates.

A parallel experiment was made in which 4 grams of common salt (2 per cent of the flour) were added to the water before mixing.

TABLE VI. EFFECT OF TIME OF DIGESTION OF FLOUR SUSPENSIONS ON DEVELOPMENT OF DIASTATIC ENZYMES

No Salt: Time of maceration	No Salt: Degrees Lintner	Salt Present: Time of maceration	Salt Present: Degrees Lintner
Minutes[a]		*Minutes*[a]	
HARD FLOUR			
2	22.4	2	81.0
16	60.7	16	97.3
31	63.6	31	98.4
46	59.5	46	98.4
61	51.0	61	101.6
76	38.3	76	101.6
91	33.8	91	103.4
SOFT FLOUR			
2	30.6	2	61.5
16	43.6	16	73.4
31	44.4	31	74.6
46	36.3	46	74.6
61	35.0	61	77.9
76	33.4	76	76.2
91	32.6	91	77.0

[a] This included the time required for filtering (only 10 cc. of filtrate was necessary for the determination of the diastatic activity).

Both hard and soft flour thus released part of the diastase and then reabsorbed it. When salt was present, the full diastatic power was released rapidly, and no reabsorption occurred.

EXPERIMENTS ON MALT

Similar experiments to those made with flour were made with barley malt. The effect of different amounts of salt was first studied. Amounts of sodium chloride ranging from 0.2 to 1.0 per cent were used, based on the total volume of the infusion. The details of the method were as specified in the new method for determining liquefying power (*6*).

TABLE VII. EFFECT OF NaCl ON LIQUEFYING POWER OF MALT INFUSIONS

Amount of NaCl: Based on digestion water	Amount of NaCl: Based on malt	Liquefying Power	Increase
%	%		%
...	..	90.5	..
0.2	10	153.0	69.0
0.4	20	163.0	80.1
0.6	30	165.0	82.3
0.8	40	165.0	82.3
1.0	50	165.0	82.3

TABLE VIII. EFFECT OF NaCl ON LIQUEFYING POWER OF VARIOUS MALTS

	Liquefying Power: No salt added	Liquefying Power: 0.5% NaCl added	Increase
			%
Small berry, choice distillers	182.7	228.7	25.1
Large berry, Iowa brewers	169.3	222.3	25.3
Large berry, fancy North Dakota pale brewers	148.2	203.0	36.9

Table VII shows that the effect of sodium chloride reached a practical maximum at 0.4 per cent sodium chloride, based on the volume of the infusion. The increase there was 80.1 per cent. The amount of sodium chloride based on the weight of malt was 20 per cent in this case.

Different kinds of malts were tried also in order to see whether or not the increase of the liquefying power was similar in each case when sodium chloride was added. It was found, however, that the increase varied greatly. In Table VIII three malts are listed with the liquefying power, with and without addition of sodium chloride.

It can be seen that the salt effect varies, a range of 25 to 36.9 per cent being found. In the first experiment an increase of 80 per cent was observed. The salt effect evidently varies in relation to the character of malt.

TABLE IX. EFFECT OF NaCl ON FILTRATE OF MALT INFUSIONS

	Liquefying Power: No salt added	Liquefying Power: 0.5% salt added to filtrate[a]
Small berry, choice distillers	182.7	185.3
Large berry, Iowa brewers	169.3	171.0
Large berry, North Dakota pale brewers	148.2	148.2

[a] 0.5 gram to 100 cc.

In order to prove that the effect of salts occurs only in the case where the salt is added to the unfiltered infusion, 0.5 per cent sodium chloride was added to the filtrate. The results are shown in Table IX.

These results show that sodium chloride does not have any effect when added to the filtrate.

The effect of ammonium chloride was also determined. When a 0.5 per cent ammonium chloride solution was used to prepare the infusion, a liquefying power of 161.5 was found, compared with a liquefying power of 90.9 on the straight malt. Thus the increase in this case was 77.6 per cent, practically the same as found with sodium chloride in the first experiment (80–82 per cent).

Since the experiments with sodium chloride showed a considerable increase in the development of the liquefying enzyme, the next study was to determine whether or not the enzyme development would occur in the same manner in mashes at higher concentrations. Two hundred grams of the finely ground malt were mashed with 600 cc. of water at room temperature, containing 0.0, 1.2, 2.4, 3.6, 4.8, and 6.0 grams of sodium chloride, respectively, corresponding to 0.0, 0.2, 0.4, 0.6, 0.8, and 1.0 per cent sodium chloride. The results are given in Table X.

TABLE X. EFFECT OF NaCl ON LIQUEFYING POWER OF MALT

Concentration of NaCl: Based on water used for infusion	Concentration of NaCl: Based on malt	Liquefying Power	Increase
%	%		%
0.0	0.0	165.0	...
0.2	0.6	168.0	1.8
0.4	1.2	170.0	3.0
0.6	1.8	172.0	4.2
0.8	2.4	172.0	4.2
1.0	3.0	172.0	4.2

These results show that only a slight increase (4.2 per cent) occurred.

To observe the simultaneous decrease of the salt effect with different mash concentrations, the following experiments were made: 20, 40, 80, 160, and 360 grams of malt were weighed in a 1000-cc. volumetric flask and filled with distilled water to the mark. Similar tests were carried out, using 5 grams of sodium chloride in each case. A portion of each filtrate was diluted to form an infusion corresponding to 10 mg. of malt in 10 cc. of the infusion. The results obtained are shown in Table XI.

TABLE XI. EFFECT OF MALT-WATER CONCENTRATION ON LIQUEFYING POWER

Malt in 1 Liter	Without NaCl: Liquefying power of infusion	Without NaCl: Liquefying power increase[a]	With NaCl: NaCl added	With NaCl: Liquefying power of infusion	With NaCl: Liquefying power increase[b]
Grams		%	% *of malt*		%
20	96	..	25.0	176	...
40	132	37.5	12.5	176	...
80	155	61.4	6.25	182	3.4
160	164	70.8	3.12	176	...
320	171	78.1	1.56	179	1.7

[a] Due to higher mash concentration.
[b] Due to higher mash concentration when NaCl is added.

These results show that increased mash concentrations increase remarkably the development of the enzyme. When 40 grams of malt were diluted to 1 liter, an increase of 37.5 per cent was observed on the liquefying power, when compared with the infusion where 20 grams of malt were diluted to 1 liter. The infusion with 320 grams of malt in 1 liter showed an increase of 78.1 per cent when compared with the infusion of 20 grams in 1 liter. The same experiments showed no appreciable increase in presence of sodium chloride, indicating that practically the same amounts of enzyme were brought into solution by sodium chloride regardless of the mash concentration. When the results obtained without and with sodium chloride are compared, it is found that sodium chloride increases the development of the enzyme in the case of lower concentration, whereas at higher concentrations the same amounts of enzyme are brought into solution regardless of the presence of sodium chloride.

Table XII shows the increase in enzyme activity in absence and presence of sodium chloride on mashes of different concentration.

TABLE XII. EFFECT OF NaCl ON VARIOUS MASH CONCENTRATIONS

MALT IN 1 LITER	LIQUEFYING POWER OF INFUSION		INCREASE
	Without NaCl	With NaCl	
Grams			%
20	96	176	83
40	132	176	33
80	155	182	17
160	164	176	7
320	171	179	5

The findings described above suggested that even carbohydrates might increase the development of the liquefying power of mashes. Different amounts of glucose (dextrose) and maltose, respectively, were added to a mash prepared from 20 grams of malt in 1000 cc. and the liquefying power observed. The results are given in Tables XIII and XIV.

TABLE XIII. EFFECT OF GLUCOSE ON DEVELOPMENT OF LIQUEFYING POWER

GLUCOSE ADDED:				
Amount	Based on wort	Based on malt	LIQUEFYING POWER	INCREASE
Grams	%	%		%
None (malt check test)	..	...	90.9	..
5	0.5	25	106.3	16.9
10	1.0	50	109.7	20.6
50	5.0	250	113.1	24.4
100	10.0	500	120.1	32.1

TABLE XIV. EFFECT OF MALTOSE AND NaCl ON DEVELOPMENT OF LIQUEFYING POWER

	LIQUEFYING POWER	INCREASE
		%
(1) Malt check test	92.6	..
(2) Same as (1) plus 0.5% NaCl	168.0	81.0
(3) Same as (1) plus 400% maltose	162.0	75.0
(4) Same as (3) plus 0.5% NaCl	172.0	86.1

These tests show that glucose and maltose were able to increase the development of the soluble enzyme in aqueous solution. Much higher concentrations of these compounds were, however, needed to develop effects similar to those of inorganic salts. The effect of glucose was less pronounced than that of maltose. Thus, 500 per cent glucose gave but 32.1 per cent increase, compared with a 75 per cent increase when but 400 per cent maltose was used. The increase of the enzyme activity when both maltose and sodium chloride were used was but 11 per cent higher than when maltose was used alone.

The effect of papain was studied in amounts of 0.05, 0.10, 0.20, and 0.50 gram in 1000 cc. wort. The amount of malt was as usual (20 grams finely ground malt in 1000 cc.). The infusion was filtered after standing 2 hours.

These tests indicated that an appreciable increase in enzyme activity could be found when papain was added to the infusion before filtering. The increase ranged from 8.0 to 60.7 per cent, a concentration of 0.05 per cent, papain giving an increase of 60.7 per cent.

TABLE XV. EFFECT OF PAPAIN ON LIQUEFYING POWER OF MALT

	AMOUNT OF PAPAIN: Based on wort	AMOUNT OF PAPAIN: Based on malt	LIQUEFYING POWER	INCREASE
	%	%		%
(1) Malt check test	...	...	92.4	..
(2) Same as (1) plus 0.05 gram papain	0.005	0.2	100.1	8.0
(3) Same as (1) plus 0.10 gram papain	0.01	0.5	101.2	9.0
(4) Same as (1) plus 0.20 gram papain	0.02	1.0	106.7	15.4
(5) Same as (1) plus 0.50 gram papain	0.05	2.5	148.5	60.7

DISCUSSION OF RESULTS

The fact that the different salts increased the concentration of soluble liquefying enzyme in the flour suspensions leads to the belief that a physical effect on the flour proteins was being measured. The fact that, while common salt increased the solubility of both liquefying and saccharifying its enzymes, its influence became less pronounced as its concentration increased, also indicates a physical effect. The solubility of both enzymes was greatly increased by papain. Here the effect was probably primarily of a chemical nature.

A marked effect of glucose and maltose upon the solubility of the liquefying enzyme of malt was found. The amounts of carbohydrates required to produce a given increase in solubility were much greater than the quantity of inorganic salt required to produce the same effect.

The results further indicate the influence of the concentration of the infusion on the solubility of both liquefying and saccharifying enzymes of flour, and on the solubility of the liquefying enzyme of malt.

For example, if one wishes to prepare a filtered infusion of malt for estimation of liquefying power of concentration such that the equivalent of 1 gram is contained in 1 liter, 10, 30, or 40 grams of sample could be mixed with a liter of water, and, after the digestion period, the sample could be filtered and 100, 50, or 25 cc. of the filtrate diluted to a liter. Each of these diluted filtrates would then correspond to 1 gram of sample. The enzyme content, however, would vary in each case, since the digestion of the different lots took place in the presence of different amounts of salt and other soluble substances in the malt capable of causing increased amounts of enzyme to pass into solution.

It is possible that this method of estimation of the liquefying power of malt, in which 20 grams of malt are digested with liter of water, should be so modified as to develop the maximum liquefying power of the sample. This, however, is a subject for further study.

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Sugar Formation by Diastatic Enzymes of Flour

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COMMERCIAL FLOURS were found to contain both liquefying and saccharifying enzymes. The addition of small quantities of salt or papain to flour suspensions greatly increased the amounts of soluble liquefying and saccharifying diastase. The presence of neither salt nor papain appreciably changed the rate of saccharification in flour.

Previous Investigations

LINTNER methods applied to flour do not give very significant results, according to Rumsey (*11*). Rumsey thinks that flour showing greater sugar-forming power should show greater strength and consequently greater baking value, providing the quality and quantity of gluten are relatively the same. He proposed a method in which the diastatic power was expressed in terms of the reducing sugar, calculated as maltose, formed when all the flour in water suspension was used to autolyze under given conditions. Although this method has been of great value in studying saccharification in flours, the relationships between the diastatic activity, as determined by Lintner methods, and saccharification remain unknown.

The earlier literature leads to the belief that the liquefying power of diastase is responsible for the direct action on the raw starch of the flour.

Brown and Morris (*3*) state, "We have always found the power to liquefy starch paste and to erode the starch granule to go hand in hand. A diastase which will liquefy starch paste will, under favorable conditions, also disintegrate the starch granule and vice versa. It is always safe to predict that a non-liquefying diastase will not attack the starch granule by pitting and disintegration, and that a diastase which will not so act on the starch granule will not liquefy starch paste."

Baker and Hulton (*1*) found an abundance of the saccharifying enzyme of diastase in flour, but they were unable to obtain the expected correlation between the diastatic power and sugar formation in doughs. The value of malt, however, in causing increased sugar for gas formation was clearly recognized. They found that as little as 0.25 per cent of malt (50 mg. for 20 grams of flour) produced a marked effect. They believed that many flours have an inadequate supply of the liquefying enzyme of diastase, and that such flours should be supplemented with malt.

Olson (*10*) held that low gas production in a weak flour is caused by an inadequate supply of starch liquefying enzyme.

Ford and Guthrie (*6*) observed the effect of the duration of extraction on the diastatic activity of flour as measured by the action of the filtered extract on soluble starch solutions. When the period of standing at 18° C. was increased from 10 minutes to 2 hours, the activity of the filtered 4 per cent suspensions decreased markedly. These investigations found that while their results were somewhat inconsistent, not surprising as the pH relations of diastase (*12*) were not known until 1915, various substances (glycine, gelatin, certain proteases, primary and secondary phosphates, and potassium chloride) greatly increased the diastatic power when added to the water in which the flour was digested. Similar effects were obtained with barley flour (*7*).

Determination of Liquefying and Saccharifying Power

The primary object of the studies reported in this paper was to apply to flour two new methods (*8*, *9*) for measuring liquefying and saccharifying power that permit the rapid and exact estimation of these components of diastase, and to relate, if possible, these enzyme activities to the sugar-forming power of flour as determined by the Rumsey method.

It was necessary to state the diastatic activities of flour in terms of grams of the substrates, starch paste, and soluble starch, used in the two methods, converted by 1 gram of the enzyme preparation. By comparing the values found with the sugar formed during saccharification in the flour by the Rumsey method, the three activities could be compared.

In the liquefying method the activity of the enzyme is measured directly in terms of substrate. The liquefying power is there defined as the weight of dry starch, in the form of a special starch paste, liquefied at 21° C. in 1 hour at 4.8 pH by 1 part of active substance.

For example, the liquefying power of a distiller's malt was found to be 128. In making the measurement, the starch paste containing 4.211 grams of dry starch per 100 grams lost 64.9 per cent of its viscosity when 150 grams of the paste were digested for 1 hour at 21° C. at 4.8 pH with 15 cc. of malt infusion, each cc. of which represented 1 mg. of malt. This loss in viscosity, represented 1.28 grams of dry starch liquefied in 100 grams of paste per hour by 10 mg. of malt infusion. Thus,

$$\text{L. P.} = \frac{1.28}{0.01} = 128$$

A substance, then, is defined as having a liquefying power of 100 when 1 part will liquefy starch paste under standard conditions at the rate of 100 times its weight of dry starch per hour.

Statement, in terms of substrate, of the activity of the saccharifying enzyme was much more difficult. The starch present in the special solution of soluble starch used in the method, in all probability, is not split quantitatively into maltose. The nearest approach to the correct solution of the problem is believed to be, to define the saccharifying power in terms of rate of formation of reducing sugar, calculated as maltose, formed when the diastase acts on the special soluble starch under the standard conditions specified in the polarimetric Lintner method (*9*).

Here the following expression was used in calculating the activity from the fall in polarization observed:

$$\text{L} = \frac{100\ D}{t \times l \times 4.6}$$

Where L = degrees Lintner
D = fall in polarization measured on sugar scale at 20° C.
t = time in hours
l = length of tube in decimeters
4.6 = constant determined experimentally

The rate of reducing sugar formation in the polarimetric method was determined by the following procedure:

Add Fehling solution, or Fehling solution and water, to a mixture of 50 cc. soluble starch solution and 5 cc. malt infusion at the end of different digestion periods. Determine reducing substances, reckoned as maltose, by the Munson and Walker method.

Determine the polarization declines in a parallel experiment, using the same procedure.

Mix 50-cc. portions of standard starch solution at 21° C. with 5-cc. portions of malt infusion also at 21° C., counting time from the moment when the first of the starch solution reaches the malt infusion.

After incubating for the desired period at 21° C., stop enzyme action by adding Fehling solution. Calculate the quantities of Fehling solution and of water added so that the 100-cc. portion later removed and boiled represents a known aliquot containing 50 cc. of Fehling solution.

The dilutions used are given in Table I.

Table I. Dilutions Used

Starch Solution Malt	Malt Infusion	Incubation Time	Fehling Solution	Water	Total Volume
Cc.	*Cc.*	*Minutes*	*Cc.*	*Cc.*	*Cc.*
50	5	0	55	0	110
50	5	15	125	70	250
50	5	30	200	145	400
50	5	45	250	195	500
50	5	60	300	245	600

The quantities of reducing sugars, as maltose, and the polarizations, are given in Table II.

Table II. Reducing Sugars and Polarizations

Incubation Time	Cu_2O	Maltose	Total Maltose	Maltose Formed	Polarization (20° C. 4-dcm. Tube)	Polarization Declines	Maltose Formed per 1° V. (4-dcm. Tube) Decline in Polarization
Minutes	*Gram*	*Gram*	*Grams*	*Grams*	*° V.*	*° V.*	*Gram*
0	0.1526	0.1189	0.1308	....	90.0	..	...
15	0.3566	0.2803	0.7008	0.5700	84.0	6.0	0.095
30	0.3851	0.3027	1.2108	1.0800	78.7	11.2	0.096
45	0.3850	0.3027	1.5135	1.3827	75.9	14.1	0.098
60	0.3407	0.2678	1.6068	1.4760	74.9	15.1	0.098

The results in Table II show that the development of reducing power, calculated as maltose, during the early stages of digestion of soluble starch by malt diastase closely parallels the declines in polarization.

The percentage of starch solids was determined by drying 10-cc. samples of the starch solution used in this work in vacuum at 70° C. before the buffer solution was added. The dry matter was 4.737 grams per 100 cc. After the buffer (2 cc. per 100 cc.) was added the dry starch present, calculated from the foregoing figures, was 4.427 grams per 100 cc.

The results are shown graphically in Figure 1.

The quantities of reducing substance calculated as maltose formed per degree of polarization decline during the first 15- and 30-minute intervals, when these declines were nearly linear, were 0.095 and 0.096 gram. If the average value, 0.0955, be accepted as correct, the saccharifying power determined by the polarimetric method can be stated in terms of rate of formation of reducing sugars.

When 5 cc. of an infusion of diastase equivalent to 250 mg. of a malt of 100° Lintner acts on 50 cc. of a soluble starch containing 2.213 grams of starch solids, under standard conditions (21° C. and 4.8 pH), the time being so chosen that the fall in polarization with respect to time is linear, the rate of fall of polarization measured in a 4-dcm. tube is 18.4° V. per hour. This corresponds to the formation rate of 1.757 grams (18.4 × 0.0955) of reducing carbohydrate calculated as maltose.

Thus, 1 gram of malt, or other substance, of 100° L. acting on soluble starch under the conditions of the polarimetric method produces reducing substances at the rate of 7.029 grams of reducing sugar as maltose per hour. When determined by the polarimetric method, then, saccharifying power is expressed in terms of enzyme and apparent sugar formed from substrate.

Under the conditions of the two methods a malt having a liquefying power (L. P.) of 100 will liquefy starch paste at the rate of 100 times its weight per hour and 1 gram of a malt having a Lintner value of 100 will produce sugar from soluble starch at the rate of 7.029 grams of reducing substance, calculated as maltose, per hour.

In using the liquefying power method, 10 grams of flour were mixed with 100 cc. of water for 1 minute by a high-speed laboratory stirrer. The flour suspension was allowed to stand for 1 hour at laboratory temperature, with occasional mixing, and poured on a folded filter. (This method of preparing the infusion differs from that used in preparing the infusion in case of malt, which is about 100 times more active.) Then 15-cc. portions of the filtrate were mixed with 150 grams of the standard starch paste and the viscosity was determined.

In the application of the polarimetric Lintner method the infusions of flour and water were made up in substantially the same manner, except that the high-speed stirrer was not used. Twenty-five grams of flour were shaken with 250 cc. of water in Erlenmeyer flasks, let stand for an hour, and filtered. In each determination 5-cc. portions of the filtrate were used.

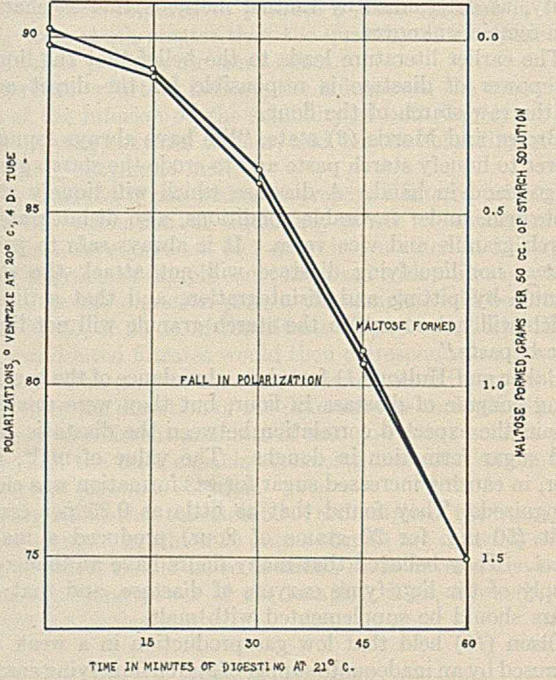

Figure 1. Relation between Fall in Polymerization and Reducing Sugar Formed during Digestion of Starch by Malt Diastase (Polarimetric Lintner Method)

These two methods were applied to the flours with and without the addition of salt. The salt (2.5 per cent and 2.0 per cent of the flour, in case of the liquefying and saccharifying powers) was dissolved in the water used in mixing.

Sugar formation in the flours was determined by a slight modification of the Rumsey (*11*) method, the details of which follow:

Mix 25 grams of flour with 241.5 cc. of water at 27° C. and let stand for 1 hour, with occasional mixing, at 27° C. Add 7.5 cc. of a solution of sodium tungstate containing 15 grams per 100 cc. and 1 cc. of concentrated sulfuric acid. After thorough mixing filter the suspension and determine the reducing sugar on 50-cc. portions of the filtrate by the Munson and Walker method. Following Rumsey's suggestion, add to the Fehling

Table III. Liquefying and Saccharifying Power of 11 Flours

Type of Flour	Liquefying Power			Saccharifying Power			Reducing Substance as Maltose[a]		
	No salt present	2.5% salt present	Increase	No salt present	2% salt present	Increase	Check	Incubated	Maltose apparently formed
			%	° L.	° L.	%	%	%	%
1. Patent from choice hard spring wheat	0.750	0.950	26	26	97	273	1.083	1.835	0.752
2. Short patent from hard winter Kansas wheat	0.780	1.220	56	23	73	218	0.881	1.989	1.108
3. Same as No. 2, unbleached	0.845	1.240	46	29	75	159	0.844	2.397	1.553
4. Northwestern flour from spring Montana wheat	0.715	1.000	39	27	80	196	1.092	2.588	1.496
5. First patent from blend of spring and Kansas wheat	0.747	1.100	47	35	96	191	1.155	2.744	1.589
6. Patent from northern spring wheat	0.850	1.097	29	26	81	211	1.154	2.678	1.524
7. First clear flour from Kansas hard winter wheat (the clear flour from the same wheat from which No. 2 was made)	0.855	1.125	31	56	89	60	1.020	2.018	0.998
8. Very short patent soft winter wheat flour	0.840	1.100	31	35	80	129	0.997	1.945	0.948
9. Patent from mixture of high-protein Kansas wheat	0.745	1.050	41	24	87	262	1.413	2.437	1.024
10. Cake flour from soft winter wheat	0.915	1.240	35	62	116	87	0.907	1.912	1.005
11. Whole wheat flour from Northern hard spring wheat	1.550	1.700	9	77	91	18	1.496	2.693	1.197
Average of flours 1 to 10	0.804	1.11	38	34.1	88.4	160	1.055	2.254	1.200

[a] Determined by Rumsey Method (*11*).

solution enough concentrated soda solution to neutralize the 0.2 cc. of sulfuric acid present in 50 cc. of filtrate. In case of the checks (determinations in which the reducing power of the original flours is measured) mix each 25-gram sample with a solution consisting of 241.5 cc. of water, 7.5 cc. of tungstate solution, and 1 cc. of sulfuric acid.

Rumsey used a 1:10 ratio of flour to water and centrifugalized instead of filtering the suspensions.

Table III shows the liquefying power of 11 commercial flours, the saccharifying power of the flours, and the sugar present in 1:10 flour suspensions before and after incubation by the Rumsey method. In all cases filtrates of the flour suspensions were used.

The results in Table III show that all the flours possessed high liquefying and saccharifying power. Omitting the whole wheat flour, the average liquefying power of the flour filtrates was 0.804. In the presence of 2.5 per cent of salt this increased to 1.11. On the average, enough power to liquefy 80.4 grams of starch paste, or 111 grams of starch paste in the presence of salt, under the standard conditions of the method, was present in each 100 grams of flour. Similarly, the average saccharifying power of the 10 flour filtrates was 33.1° L. without salt, and 88.4° L. with salt (2 per cent of the flour). This activity corresponds to the power of forming 240 and 621 parts of sugar as maltose, under the conditions of the method, from every 100 parts of flour. The average formation of reducing sugar as maltose at 27° C. in the 10 flours was only 1.20 per cent.

No correlation was apparent between either the liquefying or saccharifying power and saccharification. For example, flour No. 4 (L. P., 0.715) developed more sugar, 1.496 per cent, than flour No. 10 (L. P., 0.915), which formed 1.005 per cent of sugar. Again, flour No. 7 (56° L.) formed less sugar than flour No. 4 (27° L.).

The effect of the salt on the liquefying and saccharifying powers of the flour filtrates was striking. Increases of 26 to 56 per cent (average, 38 per cent) in liquefying power were observed. The saccharifying powers were affected to a much greater extent, the increases ranging from 60 to 273 per cent (average, 160 per cent). In case of the whole wheat flour, the increases in liquefying and saccharifying powers of the filtrates due to salt were much less (9 and 18 per cent).

Effect of Papain and Salt on Liquefying and Saccharifying Power

The remarkable effect of malt in increasing sugar formation in doughs shown by Baker and Hulton (*1*) has been repeatedly observed by others (*4*, *5*). Ford and Guthrie (*6*, *7*) showed the influence of papain in increasing the solubility of the diastases of wheat and barley flour. Baker and Hulton (*2*) reported an extended investigation of the attack of precipitated malt diastase on raw barley starch.

To determine whether or not the rate of attack of the enzymes of malt on the starch of flour could be increased by the presence of papain or salt, sugar formation in flour suspensions containing added diastatically active malt sirup was measured. Hard flour No. 6 and soft flour No. 8 were used. The amount of malt sirup (Lintner) used was 4 per cent of the flour; of papain, 0.25 per cent; and of salt, 2 per cent.

In each experiment malt sirup alone, malt sirup and papain, and malt sirup and salt were dissolved in water to a total volume of 241.5 cc., warmed to 27° C., and mixed with 25 grams of flour. The reducing substances formed upon incubating for 1 hour at 27° C. were determined by the modified Rumsey method. The results are given in Table IV.

Table IV. Reducing Substances as Maltose

Malt Sirup	Papain	Salt	Reducing Sugars as Maltose			
			Checks (not incubated)	Incubated	Increase	Increase due to papain and to papain and salt
Gram	Gram	Gram	Grams	Grams	Grams	Gram
			HARD FLOUR NO. 6			
0	0	0	0.34	1.68	1.33	..
1	0	0	3.08	7.82	4.74	..
1	0.0625	0	..	7.14	4.07	0
1	0	0.5	..	7.72	4.64	0
1	0.0625	0.5	..	7.90	4.82	0.08
			SOFT FLOUR NO. 8			
0	0	0	0.27	1.30	1.03	..
1	0	0	3.05	6.52	3.48	..
1	0.0625	0	..	6.89	3.85	0.37
1	0	0.5	..	6.13	3.08	0
1	0.0625	0.5	..	6.69	3.65	0.17

The remarkable effect of diastatic malt sirup on sugar formation in flours is clearly brought out by the results in Table IV. The hard flour formed 4.74 grams and the soft flour 3.48 grams of reducing substances reckoned as maltose. Neither papain nor salt, alone or together, appreciably increased the rate of attack of the diastatic enzymes present on the raw starch of the flours.

Conclusions

Neither the liquefying power nor the saccharifying power of diastase, using starch paste or a solution of soluble starch, has any direct bearing on the effective diastatic properties of flour. The idea that the liquefying power is concerned directly with the attack of diastase on the raw starch of flour therefore must be abandoned.

The work here reported shows that commercial flours have both types of diastatic power in excess. It shows also that the presence of salt or papain in flour suspensions effects no substantial changes in the rate of the attack on the raw starch of flour. The effect of malt extracts on sugar formation found by previous investigators was confirmed.

Acknowledgments

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Diastatic Enzymes in Certain Foods

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Although the power to liquefy starch paste is usually considered a specific function of diastase, only recently has it been possible readily to measure this property with a satisfactory degree of exactness. The new method (*5*) is rapid and exact, and its results are expressed directly in terms of substrate (anhydrous starch) and enzyme. Thus, a liquefying power of 100 means that 100 parts of dry starch in the form of standard starch paste are liquefied by 1 part of enzyme sample under the prescribed conditions.

The object of the work here reported was to obtain an idea of the distribution of the diastatic enzymes, especially the starch-liquefying enzyme, in various food crops, at the same time measuring the influence of salt.

In determining the liquefying power of the samples, 20 grams of fine-ground seeds or 50 grams of fine-ground vegetables were digested with 100 cc. of water alone and with 100 cc. of water containing 5 grams of sodium chloride per liter for 1 hour at room temperature. The solutions were then filtered and the liquefying power was determined in the usual manner.

Table I. Starch Liquefying and Saccharifying Power of Seeds

Seeds	Liquefying Power Without NaCl	Liquefying Power With NaCl	Saccharifying Power Without NaCl	Saccharifying Power With NaCl
			° *L.*	° *L.*
Soy beans, Mammoth Yellow	4.00	4.35	121	115
Cow peas, black-eye	1.15	0.90	Inactive	...
Peas, Henderson's New Jubilant	0.30	1.00	Inactive	...
Beans, Scarlet Runner, pole	0.10	1.25	Inactive	...
White lupines	1.25	2.10	Inactive	...
Lentils	3.20	3.60	Inactive	...
Japanese buckwheat	0.90	1.35	Inactive	...
Kafir corn	4.35	4.60	Inactive	...
Rice, Blue Rose[a]	2.60	3.20	Inactive	...
Field corn, New Eureka Dent	2.10	2.75	Inactive	...
Field corn, Flint Longfellow	1.65	2.10	Inactive	...
Sweet corn, Golden Bantam	1.40	2.35	Inactive	...
Sweet corn, Stowell's Evergreen	0.25	0.65	Inactive	...
Spring rye	5.75	7.80	67	76
Oats, Storm King	0.90	2.30	1	2
Barley	3.45	5.40	64	67
Malted barley	90.0	164.0	160	...
Wheat, spring, Marquis	3.40	5.15	78	96

[a] Seed rice, supplied by Chambliss, U. S. Department of Agriculture.

In determining the saccharifying power, 5 grams of fine-ground sample were digested for 1 hour at room temperature with 100 cc. of water alone, and, if the sample showed diastatic activity, with 100 cc. of water containing 0.5 gram of sodium chloride, the procedure already outlined by the writers (*3*) was followed.

The products used were not previously sterilized, nor was toluene or other preservative used during these digestions. It is possible, therefore, that some of the activities measured were due to microörganisms.

The results are given in Tables I and II.

All the seeds and vegetables showed marked liquefying action of starch paste, varying from 0.10 for Scarlet Runner beans to 5.75 for rye. The high liquefying activity of unmalted rye is interesting because malted rye is known (*1*) to have the highest liquefying power recorded for malted grains. In all products tested, except cow peas, the presence of salt increased the liquefying power. With potatoes this increase was only slight (0.26 to 0.42). With other materials it was very great, the liquefying power of Scarlet Runner beans, for example, increasing from 0.1 to 1.25.

Of the legumes listed, soy beans alone exhibited any saccharifying power. Here, however, the activity found, 121° L., was of the same order as that of barley and malt. Buckwheat, kafir corn, field and sweet corn, and rice were substantially lacking in saccharifying power, and oats showed only 1° L. Salt increased the saccharifying power in all the active materials except that from soy beans.

The results as a whole reveal an ability to liquefy starch paste widely distributed in food plants. Whether this liquefaction is the action of a phosphatase (*6*) or a necessary step in the digestion of starch by the saccharifying enzymes of plants and animals is not known. This function of diastase is of great importance in the digestion of starch because of the enormous quantities of starch metabolized by plants and animals. The cause of the influence of salt is unknown.

Table II. Starch Liquefying and Saccharifying Power of Vegetables

Vegetables	Liquefying Power Without NaCl	Liquefying Power With NaCl	Saccharifying Power Without NaCl	Saccharifying Power With NaCl
			° *L.*	° *L.*
Jersey potatoes	1.48	2.14	31	36
Turnip rutabaga	2.64	2.84	[a]	..
Parsnips	1.10	1.60	[a]	..
New potatoes	0.26	0.42	[a]	..
Carrots	0.40	0.78	[a]	..

[a] No activity.

From the data here given the saccharifying power seems to be far less widely distributed in plant products than the liquefying power of diastase.

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Factors Influencing Properties of Isolated Wood Lignin

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TEMPERATURE, acid concentration, and length of time of the reaction must be controlled in order to obtain, by the sulfuric acid method, lignin as unchanged as possible.

When lignin was isolated by the Freudenberg method some of it was lost by the sodium hydroxide and the copper ammonium solution extractions.

Conditions that produced the lowest yield of lignin by the sulfuric acid method also gave the highest yield of hydrolyzed carbohydrates.

Lignin isolated by 70 per cent sulfuric acid at 10° C. for 16 hours was free from carbohydrates, gave a higher methoxyl content, and was more readily methylated than lignin isolated by other methods.

ONE cause of the comparatively slow progress in lignin chemistry is the difficulty of obtaining lignin free from other plant tissues and unchanged in the process of isolation. Practically every process that has been advanced is open to objection. Two general methods are now in use: The removal of all the constituents of the cell except the lignin; and the extraction of lignin from the cell. The former, the only one considered in this paper, depends on the fact that the carbohydrate constituents dissolve in certain solvents, the most commonly used of which are strong hydrochloric acid, sulfuric acid, and copper ammonium solution. Upon further hydrolysis of the diluted acid solutions the carbohydrates are converted into simple sugars, which may be washed out with water.

The reaction with hydrochloric acid was worked out by Willstatter and Zechmeister (*25*) and modified slightly by Kalb (*24*) and Hagglund (*8*). The lignin obtained with this reaction was found by Kalb and Lieser (*11*) to contain residues of cellulose and by Du Pont (*3*) to contain pentosans. When the reaction is continued for a longer time a number of side reactions take place, giving an insoluble product incapable of methylation and containing decomposition products of the wood carbohydrates (*11*).

The copper ammonium solution method of obtaining lignin, that of Freudenberg and Harder (*6, 7*), gives a tan product uniform in appearance and crumbly. This material represents only the less soluble portion of the lignin present in the wood, as lignin is also soluble in the copper ammonium solution (*11, 23*). The isolation is such that it is almost impossible to remove all of the carbohydrate material from the sample. A sample of maple lignin prepared by this method at the Forest Products Laboratory gave about 70 per cent of the yield obtained by the standard laboratory method, but still contained about 5 per cent cellulose and 2.5 per cent pentosans and had a much lower methoxy content than was expected.

The sulfuric acid method was developed by Flechsig (*5*) and others (*13, 15*) as an analytical method to determine lignin content of wood. It was later modified by Klason (*12*), Becker (*1*), Mahood and Cable (*14*), Bray (*2*), and Venkateswaren (*22*). This method has several objections. Palocheimo (*16*) states that long exposure to sulfuric acid causes humus formation and too short a treatment leaves carbohydrates. Euler (*4*) found a loss of acetic acid and absorption of sulfuric acid. Freudenberg and Harder (*6*) contend that formaldehyde is split from lignin by the action of acid. On the other hand, the sulfuric acid method has advantages in that the desired concentration is easily obtained by diluting the concentrated acid. It is also easier to duplicate results with the sulfuric acid method than with any other now in use, except perhaps the modification of this method by Ross and Hill (*20*). The Ross and Hill modified method, however, would never be used for isolating pure lignin because of the possibility of resin formation between formaldehyde and lignin (*21*). Sulfuric acid also has the advantage of being rapid and requiring only one treatment. Loss of acetic acid and formaldehyde may be reduced by keeping the temperature low.

Experimental Isolation of Lignin

Sugar maple was selected as the wood from which to prepare lignin. Wood free from bark and knots was ground to 60–80 mesh fineness and air-dried, then extracted with alcohol-benzene (1–2) for 50 to 60 hours in a Soxhlet apparatus. After drying to remove the alcohol-benzene, the sample was extracted with cold and hot water for several hours. Loss in weight by these extractions was 13 per cent. This value is higher than that found by Ritter and Fleck (*18*) for ether extractive.

Lignin was isolated by each of the three methods described. The Willstatter (*25*) method gave a dark green product with a yield of 21.2 per cent. Boiling with water, according to the method of Rassow and Zickman (*17*), had no effect on the color of the product. The Freudenberg lignin (*6*) was light tan in color, gave 14.7 per cent yield on the basis of air-dried wood, and contained 15 per cent methoxyl as determined by the Zeisel method. Sulfuric acid lignin, prepared by the standard Forest Products Laboratory method (*2*), was dark in color and contained absorbed sulfuric acid. The average yield in several determinations was 23.5 per cent.

The fact that the sulfuric acid lignin was so dark in color and that the yield was greater than that produced by hydrochloric acid seemed to indicate that carbohydrate decomposition products were present in the residue and that decomposition of the sugars, as well as hydrolysis of the carbohydrates, took place. The comparative ease with which carbohydrates may be converted into a lignin-like substance (*10*) at elevated temperatures suggested that the same effect may be produced when sulfuric acid comes in contact with the wood. A series of experiments, therefore, was made on Cross and Bevan maple cellulose to determine the rise in temperature, the tendency to char, the residue formed under various conditions, the relative speed of the reaction of solution and hydrolysis, and the effect of the concentration of the acid at different temperatures.

Rise in Temperature by Action of Sulfuric Acid

Samples of 2 grams of wood cellulose were treated with 70 per cent and 72 per cent acid at 0°, 10°, and 25° C. The rise in temperature at 10° and 25° C. with 70 per cent acid was about 6 degrees, while that with 72 per cent was 8 to 10 degrees. With both concentrations the temperature rise at 0° was almost negligible because the reaction was very slow. Maple sawdust treated under the same conditions gave similar results (Table I).

TABLE I. MAXIMUM TEMPERATURE IN TREATING SAWDUST WITH H_2SO_4 AT VARIOUS TEMPERATURES[a]

CONCENTRATION OF ACID	TEMP. OF REACTION			
%	° C.	° C.	° C.	° C.
0	5	10	20	25
70	11	16	26	30
72	16	20	30	32

[a] Two grams of sawdust were used.

The greater rise in temperature with the 72 per cent acid is thought to be due to the greater speed of the reaction. As shown in Table V, the lowest yields were obtained where the temperature of the initial reaction did not get higher than 17° C.

CHARRING ACTION OF SULFURIC ACID

Solutions of cellulose and 72 per cent sulfuric acid were allowed to stand to determine the time when charring began. At 0° C. the solution was still colorless after 72 hours; at 5° C. slight charring took place within 48 hours; at 10° C. charring took place within 16 hours; and at 25° C. charring developed in less than 15 minutes. That this charring produced a lignin-like residue was determined by hydrolyzing the solutions. The sample at 0° for 36 hours gave 0.08 per cent residue; at 25° for 16 hours, 0.80 per cent; and at 25° for 36 hours, 3.0 per cent residue. These residues, after chlorination, were soluble in sulfite solution. This indicated that the dark color and higher yield of lignin with sulfuric were caused by decomposition of the carbohydrates in the wood.

SPEED OF SOLUTIONS AND HYDROLYSIS

As charring developed under some conditions from the action of sulfuric acid on cellulose, it was desirable to know the time required for the solution of the cellulose. To determine this the action of sulfuric acid on maple cellulose was studied with various acid concentrations.

TABLE II. TIME REQUIRED FOR CELLULOSE[a] TO LOSE GELATINOUS PROPERTY AT DIFFERENT TEMPERATURES

H_2SO_4 CONCN.	LENGTH OF TIME AT:		
	5° C.	10° C.	25° C.
%	*Minutes*	*Minutes*	*Minutes*
80	30[b]	[b]	[b]
75	50	20[b]	10[b]
72	120	30	15[b]
70	180	60	25[b]
68	250	90	35
65	500	210	60
60	[c]	[c]	[c]

[a] One gram in 15 cc. H_2SO_4.
[b] Charring.
[c] No solution.

The higher concentrations and temperatures produced charring and, therefore, were unsatisfactory, while the lower concentrations did not dissolve the cellulose. The lower solutions, if diluted with water and boiled, gave a precipitate of unhydrolyzed cellulose. Therefore, it was necessary to let the solution stand until the hydrolytic products remained in solution on dilution and boiling (Table III).

TABLE III. TIME NECESSARY TO GIVE A SOLUTION IN WHICH NO CELLULOSE REMAINS AFTER BOILING 4 HOURS WITH 3 PER CENT SULFURIC ACID

ACID CONCN.	TIME REQUIRED AT:		
	5° C.	10° C.	25° C.
%	*Hours*	*Hours*	*Hours*
68	16–20	10–16	7–10
70	16–20	10–16	7–8
72	8–16	8–10	[a]

[a] Charring.

To determine the conditions for the most complete hydrolysis of the carbohydrates in the cellulose solutions, samples of the boiled, diluted solutions were analyzed for reducing sugars. With 68 per cent acid at 10° C. for 16 hours, the value was low, indicating incomplete hydrolysis. With 70 per cent acid at 10° C., the value was very near that expected from theory. With 72 per cent acid at 10° and 20° C., in which charring was obtained, the value was again low, indicating decomposition of the carbohydrates. At least 16 hours, therefore, were required for solution at 10° C. for the 70 per cent sulfuric acid.

Two reactions were considered as taking place, namely, hydrolysis and decomposition. At the higher concentrations of acid both occurred at the same time. Later experiments were carried out to determine the conditions for the most complete hydrolysis and the least decomposition. This condition should give a high sugar-reducing number and a low lignin residue. Both of these occur with 70 per cent acid at 10° C. for 16 hours. Table IV shows the effect of temperature and time of reaction on the yield of lignin with 72 per cent sulfuric acid. After hydrolysis the solution in each case was diluted to 3 per cent acid concentration, boiled for 4 hours, and filtered through an alundum crucible.

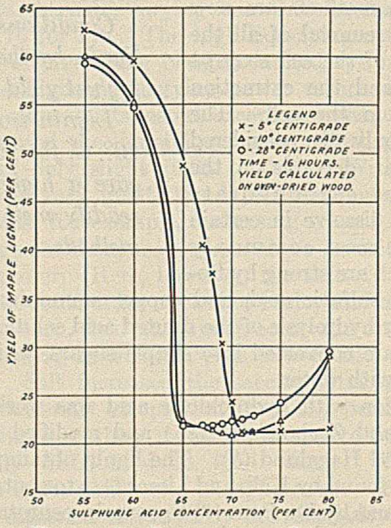

FIGURE 1. ISOLATION OF LIGNIN

TABLE IV. LIGNIN BY 72 PER CENT ACID AT VARIOUS TEMPERATURES AND INTERVALS

INTERVAL	AVERAGE YIELD AT:			
	−20° C.	0° C.	10° C.	25° C.
Hours	%	%	%	%
7	..	[a]	21.2	21.6
16	..	23.8	21.8	22.7[b]
36	..	21.1	23.8[d]	28.0[c]
48	[a]	21.1	27.0[c]	40.0[c]
500	[e]	[c]	[c]	[c]

[a] Gelatinization. [b] Dark. [c] Charred. [d] Dark. [e] Incomplete solution.

The material prepared at 0° for 36 to 40 hours, or at 10° for 7 to 16 hours, was easily filtered, was light tan in color, settled out to form a clear solution, and, on drying, formed a dry amorphous powder. These observations are contrary to the findings of Harlow (*9*), who reported that hardwood lignin filtered with difficulty and dried to a hard cake. Lignin prepared at higher temperatures or over a longer time, however, did have the properties described by Harlow. This may be due to the decomposition products of the carbohydrates that remain in the residue. The results of an experiment similar to that just described, but with the acid concentration varied and the time constant, are shown in Table V and Figure 1.

TABLE V. LIGNIN ISOLATED AT VARIOUS ACID CONCENTRATIONS AND TEMPERATURES

(Time, 16 hours; yield calculated on oven-dried wood)

H_2SO_4 CONCN.	AVERAGE YIELD AT: 5° C.	10° C.	28° C.
%	%	%	%
80	21.4	29.0	29.5
75	21.3	22.2	24.1
72	21.1	21.2	22.8
71	21.1	21.0	22.5
70	24.2	20.8	22.3
69	30.3	21.0	22.0
68	37.5	21.4	21.7
67	40.4	21.7	21.7
65	48.8	22.0	21.7
60	59.5	55.5	54.8
55	62.8	60.0	59.2

The product from the higher concentrations and temperatures was black, filtered very slowly, and, on drying, formed a hard brittle mass. With the lower concentrations (55 and 60 per cent) the appearance of the wood changed very little. The product isolated at 10° C. with 70 per cent acid seemed the most desirable because it gave the lowest yield, was freest from charred decomposition products, and, as determined by solubility with chlorine and sulfite solution, was free from cellulose. The sample isolated at 10° C. with 68 per cent acid contained a small amount of cellulose. A sample prepared at room temperature and at the same concentration as used by Klason (*12*) was not so satisfactory because the yield was almost 1 per cent higher and the product was darker than in the case of that obtained at 10° C. and 70 per cent acid. More recently, Ritter and Seborg (*19*) have applied these effects of time and temperature with 72 per cent sulfuric acid on the quantitative yield of lignin from wood and have suggested the reduction of time from 16 to 2 hours.

ISOLATION OF LIGNIN WITH SULFURIC ACID

These experiments showed that the following procedure for the isolation of lignin with sulfuric acid is satisfactory:

Add a sample of alcohol-benzene and water-extracted sawdust (60-80 mesh) weighing 8 grams (equivalent to 8.65 grams of original sawdust) to 80 cc. of 70 per cent acid previously cooled in a stoppered flask to 10° C. Shake the flask until gelatinization occurs (about 3 minutes) and return to the cooling bath. After about an hour, when the mixture begins to thin, shake again for a few minutes to insure contact of the acid with all the sawdust. After 16 hours in the cooling bath at 10° C., pour the contents of the flask into a 4-liter flask containing 2 liters of cold water. Wash the sulfuric acid mixture remaining into the flask with cold water and fill the flask up to 3 liters. Then mix the contents of the flask well to prevent superheating of the residue in contact with strong acid which otherwise would cause the loss of the formaldehyde group (*6*). Boil the dilute acid mixture for 4 hours under a reflux condenser, allow it to settle, and decant through an alundum crucible. Wash the residue into the crucible with 1 liter of hot water to remove adsorbed sulfuric acid. When the filtering and washing are complete (usually in 15 minutes) dry the residue at room temperature to about 9 per cent moisture content. For experimental work it was found more satisfactory to work with the product at 9 per cent moisture content than at lower moisture content values because oven-drying gave a less reactive and darker product. The average yield from several runs was 20.8 per cent of lignin (oven-dry basis).

The product thus isolated was found to contain 21.0 per cent methoxyl by Zeisel. After two methylations with dimethyl sulfate the product was very near the original sawdust in color and contained 32.5 per cent methoxyl.

The product isolated at room temperature with 72 per cent acid contained 17.1 per cent methoxyl and, on being methylated twice, contained 22.8 per cent methoxyl. The methylated product was still dark brown. Further methylation produced no increase in methoxyl content.

The original wood contained 5.3 per cent methoxyl. The isolated lignin contained 82.4 per cent of this, which, as far as the authors are aware, is as high a yield of methoxyl as any reported (*8*). Lignin isolated by the Freudenberg method contained only 41 per cent of the methoxyl of the original wood. Some of the methoxyl-containing material was removed by the extraction with cold 5 per cent sodium hydroxide in the Freudenberg method, as this extract gave a residue similar to lignin when treated with sulfuric acid and contained methoxyl groups. Wood sawdust previously treated with cold 5 per cent sodium hydroxide before the isolation by 70 per cent acid yielded 17.3 per cent lignin of approximately the same methoxyl content. This indicated a loss of almost a fifth of the lignin by sodium hydroxide extraction alone.

DISCUSSION

In the isolation of lignin by sulfuric acid in as unchanged form as possible, it is necessary to control conditions to prevent secondary reactions which bring about decomposition of dissolved carbohydrates. Temperature is one of the most important factors, as a few degrees greatly change the speed of the two reactions, decomposition apparently being hastened more than hydrolysis. At low temperatures very little decomposition occurs, even in long periods. Moderate acid concentrations have advantages over higher concentrations in that the rise in temperature when the acid comes in contact with the sawdust is less, and the charring action therefore less, while the speed of hydrolysis is but slightly retarded. If the acid is allowed to remain in contact with the hydrolyzed carbohydrates for long periods decomposition takes place. If the time is too short, hydrolysis is incomplete. The highest yield of sugar from hydrolysis should indicate the point where the greatest amount of cellulose is hydrolyzed and the smallest amount of sugars decomposed. It should also be the point where the lowest yield of lignin is obtained. A low lignin yield, therefore, is considered an index to the extent of decomposition.

In the method for isolating lignin used by Freudenberg (*7*), the extraction of the sawdust with alkali is open to question because lignin is dissolved, as shown by the fact that this extract gives a lignin-like residue that contains methoxyl, and the lignin yield by sulfuric acid from alkali-extracted sawdust is decreased by almost a fifth, while the methoxyl ratio is unchanged.

If the percentage of methoxyl in the isolated lignin may be considered as a check on the purity, sulfuric acid under controlled conditions produces lignin of higher quality than that produced by other methods. Sulfuric acid lignin better represents the lignin of the wood because it contains a high percentage of the total methoxyl found in the wood.

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Seasonal Manganese in a Public Water Supply

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MANGANESE is produced in stored water containing carbon dioxide by leaching from the underlying soil. This carbon dioxide is produced by the fermentation of organic material left on the sides and bottom of an unstripped reservoir. During the autumn "turnover" this manganese is distributed through the water, and, by aeration, is converted into an unstable hydrated oxide.

The decomposition of dead microörganisms does not affect this condition materially. Hence copper sulfate treatment is effective only to control the taste and odor of the water.

The feasibility of stripping a reservoir for manganese control depends on the cost of the work as compared with the cost of iron and lime coagulation for a few years.

MANGANESE in a public water supply is generally conceded to be a nuisance. Low concentrations produce a grayish black stain on clothes when laundered and clog zeolite softeners and industrial pressure filters, thereby bringing complaints from bottlers, laundries, and dairies. Occasionally the average consumer protests because of stains on white enamel fixtures.

As manganese is easily oxidized, it usually occurs as an unstable hydrated oxide of uncertain composition, possibly Mn_3O_4. It is therefore easily reduced, frequently giving a false color reading for the available chlorine determination (*5*). Unless properly corrected, such a situation can readily cause a dangerous sanitary condition in the control of a water supply. A recent analytical modification of the test for manganese in the presence of manganous compounds has been published (*2*). Manganese is removed from a public water supply in the purification process by using ferrous sulfate and lime as the coagulating medium (*1*). The ferric hydroxide formed at its isoelectric point, pH 9.2 to 9.4 for this water, will completely adsorb manganous oxides (*6*, *7*).

Conditions at Baltimore

Manganese in excessive amounts is a seasonal phenomenon in the river water used as the source of supply in Baltimore, Md. The curves in Figure 1, which are weekly averages of daily analyses at the plant, show that this trouble occurs in the late autumn, reaching a maximum in October of each year. The investigation here reported was undertaken to discover the cause of this condition and to find a remedy for it.

Weekly samples of surface and bottom waters were collected from a point in the 23,000,000,000-gallon reservoir, No. 1 Bridge, approximately 50 feet deep and about 2 miles upstream from the intake at the dam. The surface samples were collected in a bottle of 1000 cc. capacity lowered from the bridges and the bottom samples in an apparatus designed for the purpose (*8*). No. 1 Bridge is about 8 miles below the head waters of the reservoir. Hence the characteristics of the water at this point would be only slightly, if at all, influenced by fluctuations of contributing stream flow. The manganese conditions at this spot are comparable to those of a deep pool under climatic and wind effects.

Manganese in Surface Water

The appearance of the manganese trouble only in the autumn and its continuing until midwinter indicates that the "seasonal turnover" of the reservoir water is a contributing factor. The curves in Figure 2 show this to be true. During the warm summer months the temperature of the bottom water gradually increased from 5° to about 20° C., the surface water being constantly about 3 to 5 degrees higher. With the beginning of colder weather, about October 1, the surface temperature fell rapidly. The temperatures were soon equalized and a gradual reduction followed, until final stagnation was reached, about December 18, at 5° C. During this period the manganese content of the surface water, which up to this time had remained at 0.01 p. p. m., increased. This increase persisted until about January 1. Using the presence of manganese in the surface water as a criterion, the belief that "this overturn continues until a period of fairly stable equilibrium known as winter stagnation is reached" (*3*) is correct. Further inspection of the curve shows that the manganese increase occurred only when the temperature fell below 15° C. This proves that the mixing of the top and bottom waters distributed the element through the reservoir.

Comparison of the water temperatures from No. 1 Bridge with those from Warren Bridge, $4^1/_2$ miles further up stream, having a depth of about 25 feet, indicates that stagnation did not occur at this point. The results in Table I, Section A, show this in detail. The results in Section B confirm the belief that while manganese is initially found in the mud on the reservoir bottom it is brought to the surface only during periods of "seasonal turnover." The data for the Paper Mill Bridge Section, with a depth of only about 10 feet, support this opinion.

Proof that manganese is obtained from the bottom water is given by the curves in Figure 3. These show clearly that at certain seasons of the year appreciable quantities of this element are present in the water. Beginning to increase the middle of June, it reaches a maximum by the middle of August, remaining fairly high until October. At the period of "seasonal turnover," about October 20, a rapid reduction in the bottom water, with a corresponding increase

TABLE I. CHARACTERISTICS OF WATER AT WARREN AND PHOENIX BRIDGES[a]

Month	Section A						Section B				Section C					
	Warren Bridge			Paper Mill Bridge			Manganese at Warren Bridge		Manganese at Paper Mill Bridge		Warren Bridge			Paper Mill Bridge[a]		
		Temperature			Temperature						pH		Dissolved O	pH		Dissolved O
	Depth	Bottom	Top	Depth	Bottom	Top	Bottom	Top	Bottom	Top	Bottom	Top	Bottom	Bottom	Top	Bottom
	Feet	*°C.*	*°C.*	*Feet*	*°C.*	*°C.*	*P. p. m.*	*P. p. m.*	*P. p. m.*	*P. p. m.*			*% Sat.*			*% Sat.*
1930, Aug.	28.5	26	26	11.5	24	25	0.26	0.01	0.44	0.11	7.0	7.4	39	6.9	7.1	65
Sept.	26.0	25	25	8.5	25	25	0.57	0.10	0.60	0.32	6.9	6.9	60	6.8	6.9	63
Oct.	24.0	16	17	6.5	16	16	1.05	0.24	0.32	0.16	7.1	7.1	68	7.1	7.2	76
Nov.	21.5	10	12	3.5	..	..	0.37	0.33	..	0.43	7.1	7.1	71	...	...	..
Dec.	19.5	5	3	2.0	..	..	0.14	0.14	..	1.20	7.1	7.0	79	...	...	..
1931, Mar.	24.0	..	..	6.0	..	..	..	0.04	..	0.08	...	...	..	...	...	..
April	26.5	..	..	9.0	..	..	..	0.02	..	0.04	...	...	..	...	...	..
May	28.0	18	21	10.0	19	19	0.13	0.05	0.26	0.12	7.1	7.4	74	6.8	7.0	73
June	28.5	23	24	11.0	24	26	0.28	0.04	0.33	0.09	6.6	7.5	51	6.8	7.1	67
July	27.5	25	29	10.0	28	29	0.65	0.04	0.30	0.13	6.6	7.6	34	6.6	7.3	62

[a] The Warren Bridge location is influenced by contributary stream flow; the Phoenix Bridge point is comparatively shallow. Figures are monthly averages of weekly samples.

in the surface samples, is observed. This proves that the water had been equally mixed. That a rapid mixing of these waters would occur is shown by reviewing any table of density in its relation to temperature change. Table II gives a few pertinent relationships.

TABLE II. DENSITY OF WATER

° C.	*Gram/cc.*
25	0.997044
20	0.998203
15	0.999099
10	0.999700
5	0.999965
4	0.999973
0	0.999841

The figures in Table II explain the sudden diffusion of manganese through the reservoir. The increase in density when the temperature falls from 25° to 15° C. is much greater (0.2 per cent) than when it falls from 15° to 4° C. (0.09 per cent). With the water quickly cooling from about 25° to 15° C. in two weeks, the density changed rapidly in conformity with these ratios, thoroughly mixing surface and bottom waters. This theory is confirmed by the finding that the maximum amount of manganese at the surface in October is intermediate between that normally found in the two waters. Additional confirmation is given by the dissolved oxygen curve in Figure 3. When the temperature fell below 15° C. an immediate increase of this element was noted in the bottom water, showing that admixture had taken place.

MANGANESE IN BOTTOM WATER

Except possibly in the colder months, manganese is always present in the bottom water in amounts above 0.1 p. p. m. (Figure 3). This increase occurs after the temperature of the bottom water has been at 20° C. or above for about 30 days. During this period a progressive reduction in the dissolved oxygen is found. This falls to a minimum of 15 per cent saturation coincident with the maximum temperature of 23° C. The curves in Figure 3 indicate a fermentation of the organic material on the reservoir bottom caused by the action of proteolytic bacteria. The carbon dioxide liberated by this process is suggested as the source of soluble manganese.

This digestion is comparable with that of organic sewage material in that it proceeds readily with a minimum amount of oxygen. A discussion (*9*) of digestion-of-sewage-sludge experiments suggests that the optimum point is at about 28° C., with a pH value from 6.8 to 7.6, and that complete digestion will take place in 30 days. As the usual temperature of the reservoir in summer is between 20° and 30° C., and the pH between 6.0 and 6.8, with the oxygen content very low, it is logical to assume that an analogous digestion occurs on the bottom. This more or less septic state easily produces excessive amounts of carbon dioxide in conjunction with other resultant gases. A comparison of the characteristics of the water at the Warren Bridge and at the Paper Mill Bridge locations supports this view (Table I). No relation in constituents between the top and bottom waters is observed. If there is an apparent sequence it does not remain for any definite period. The Warren Bridge location presents the effect of contributing stream flow and the other point only that of shallow water.

The hydrogen-ion concentrations of the top and bottom waters (Table IV) prove the presence of excessive carbon dioxide. The bottom water was decidedly more acid than the top, owing to adsorption of the gas. It remained so until the period of winter stagnation.

Water containing free carbon dioxide will dissolve hydrated manganous oxides (*5*, *10*). Therefore such water stored over an area of manganous rock deposits, particularly in deep reservoirs, will under the conditions of fermentation always contain these soluble salts in the bottom water. At the time of "seasonal turnover" this element will be distributed throughout the body and become aerated and the soluble salts will be converted into a hydrated oxide.

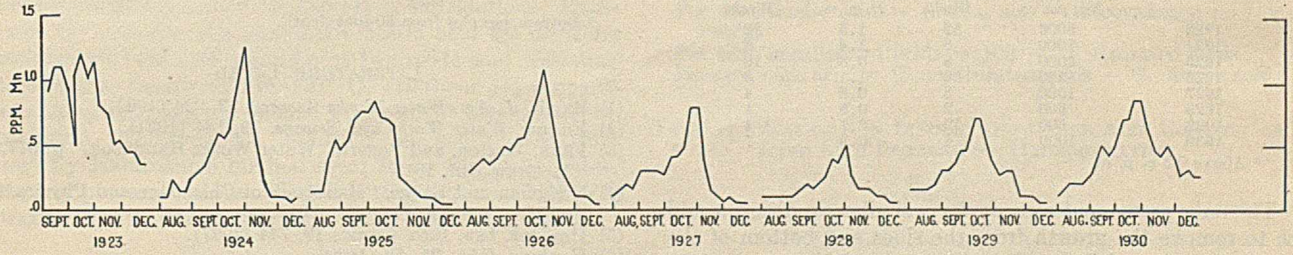

FIGURE 1. PLANT DATA, 1923–30

CORRECTION OF MANGANESE TROUBLE

The yearly curves in Figure 1 reveal a gradual decrease in the maximum amount of manganese found for each period. In 1921 a new area of land was flooded. Before flooding the top soil was not stripped or grubbed. This condition produced an abundant supply of organic material for fermentation and subsequent leaching of manganese from the soil on the bottom. The gradual decrease in the peaks of the curve indicate that with the passage of time this fermentation will be checked by silting of the bottom, thereby eliminating the trouble. The absence of silting in 1929 and 1930 by run-off is reflected in the increased peaks for those years. It is believed that with abatement of the drought and with normal rainfall the peaks will show the usual yearly drop.

Baylis (*1*) originally thought the phenomenon was due to the presence of a particular slime bacteria producing organic acids that dissolved the manganese. In recent years this organism has not been found in the water thus eliminating it as the causative agent. The possibility that decomposing microörganisms supply the organic material for digestion was considered. Table III presents the relation between periods of maximum organic content and manganese appearance in the water. These figures indicate that the increase in carbon dioxide is not a direct function of microorganism concentration. No indication was found that an extended period of moderate microörganism growth produced excessive fermentable material. It must be concluded that digestion of the excessive organic material from the unstripped reservoir bottom is the underlying cause of the trouble.

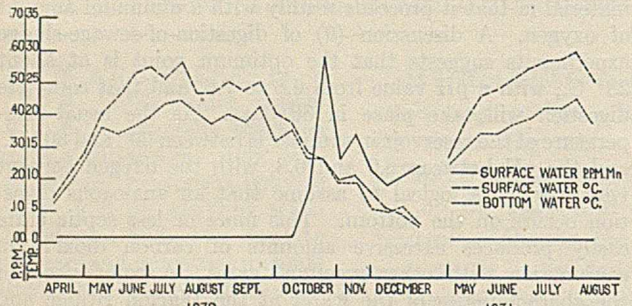

FIGURE 2. WATER AT BRIDGE No. 1

TABLE III. RELATION OF MICROÖRGANISMS TO DURATION OF MANGANESE IN WATER

YEAR	MICROÖRGANISMS Maximum	Duration	MANGANESE Maximum	Duration[a]
	No. per cc.	*Weeks*	*P. p. m.*	*Weeks*
1923	5000	52	1.3	12
1924	1000	6	1.4	8
1925	1000	8	0.8	10
1926	1500	8	1.1	8
1927	1000	8	0.8	4
1928	800	2	0.5	1
1929	500	12	0.7	4
1930	1000	4	0.9	7

[a] Above 0.5 p. p. m.

The only permanent remedy for a similar condition would be to remove the growth from the sides and bottom of the reservoir before filling. This is very widely practiced in New England, especially in Massachusetts. Digestion is reduced to a minimum, eliminating soluble manganese as a by-product. Stripping and grubbing a reservoir are expensive. This cost must be compared with that for iron and lime coagulation over a few years. If the cost of such coagulation is prohibitive in plant control for a given location, stripping would be justified. It is believed that under normal conditions manganese may be economically removed from water by coagulation methods without an undue burden on the purification process.

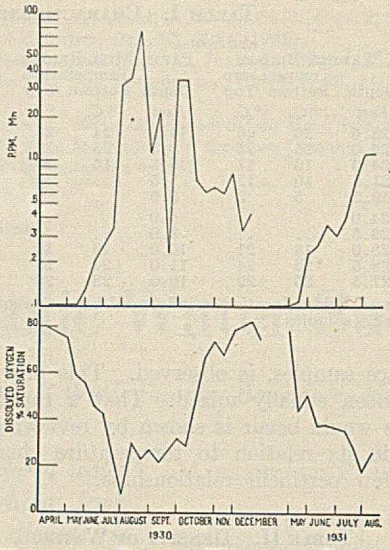

FIGURE 3. BOTTOM WATER AT BRIDGE No. 1. (50-foot depth)

TABLE IV. pH OF WATER AT No. 1 BRIDGE

(Monthly average of weekly samples)

DATE		pH Top	Bottom[a]
1930	Mar.	7.2	7.3
	April	7.1	7.1
	May	7.5	7.0
	June	7.5	6.7
	July	7.4	6.6
	Aug.	7.5	6.6
	Sept.	7.4	6.7
	Oct.	7.2	6.4
	Nov.	7.2	6.0
	Dec.	7.1	6.0
1931	May	7.5	6.4
	June	7.6	−6.0
	July	7.6	6.2
	Aug.	7.5	−6.0

[a] Bottom samples from 50-foot depth.

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POSITION OF RAYON INDUSTRY IMPROVED. The United States rayon industry, the most important factor in the world's rayon trade, will start 1932 in a much better statistical position than it entered 1931, according to the Department of Commerce.

The slashing of huge stocks that had piled up at the close of last year is one of the most important reasons for the improvement. Trade figures show that stocks have been cut from approximately 27,000,000 pounds to some 15,000,000, which is practically a normal supply.

Following a fairly active demand for rayon prior to October 1, sales have slackened, partly because the demand from weavers and knitters has fallen off and partly because of the withdrawal of guarantees. Nevertheless, the trade believes production for the year will slightly surpass that of 1930, which was approximately 115,000,000 pounds. This year's output is estimated at some 120,000,000 pounds, or just short of the 1929 record of 121,566,000 pounds.

The domestic textile industry, moreover, is relying less on foreign materials than formerly. Last year imports of rayon yarns were only 5.76 per cent of domestic production, as compared with 12.33 in 1929, 12.47 in 1928, and 19.21 in 1927. The 1931 proportion will be less than 2 per cent.

Thiocyanogen Number and Its Application to Studies on Lard

LAWRENCE ZELENY AND C. H. BAILEY, *Division of Agricultural Biochemistry, University Farm, St. Paul, Minn.*

THE technic for the quantitative determination of the addition of thiocyanogen to fats and oils was developed by Kaufmann (*5*). Thiocyanogen in solution behaves very much like the halogens; in fact, it is sometimes called a pseudohalogen. In reactivity it stands midway between bromine and iodine; it is freed by bromine from its salts, but it liberates iodine from iodides. It is immediately decomposed by water, the end products being HSCN, HCN, and H_2SO_4. In most solvents it polymerizes more or less rapidly; turbidity appears first, followed by the precipitation of a yellow amorphous mass.

Thiocyanogen adds only to certain of the double bonds of the unsaturated fatty acids, while iodine and bromine add to all such double bonds. For example, thiocyanogen adds to only one of the two double bonds of linolic acid, while it adds quantitatively to the one double bond of oleic acid. It follows, then, that for fats containing only these two unsaturated fatty acids the difference between the iodine number and the thiocyanogen number will be a measure of the linolic acid content.

Thiocyanogen solution suitable for fat analysis is prepared by adding bromine and an excess of lead thiocyanate to anhydrous acetic acid and shaking the mixture until it is decolorized. The lead bromide and excess lead thiocyanate are filtered off through a dry plaited filter, giving a perfectly clear, colorless solution of thiocyanogen. A solution about 0.05 *M* of $(SCN)_2$ is most suitable.

Kaufmann (*5*) found that the tendency for thiocyanogen to polymerize was less in acetic acid solution than in other solvents. It is of the utmost importance, however, that all reagents and glassware used be absolutely dry, as traces of moisture greatly lessen the stability of the solution. Kaufmann (*5*) prepares the anhydrous acetic acid by distilling glacial acetic acid over phosphorus pentoxide and collecting the distillate boiling at 118–120° C. Barbour (*1*) prepares the acid by refluxing glacial acid with a slight excess of acetic anhydride. Thiocyanogen solutions in acetic acid prepared by Kaufmann's method seem to be the more stable. Properly prepared solutions lose less than 1 per cent of their titration value during the first week after preparation.

EXPERIMENTAL PROCEDURE

In determining thiocyanogen numbers on lard it was found necessary to modify Kaufmann's technic in two respects. The lard is washed into the reaction flask with anhydrous ether, the ether being subsequently evaporated off. This leaves the lard in a thin film on the bottom of the flask, thus exposing a large surface to the thiocyanogen solution. This procedure is necessary because lard is relatively insoluble in acetic acid.

The reaction is allowed to proceed for 17 hours, the 5 hours suggested by Kaufmann being insufficient.

The following technic gave satisfactory and consistent results:

Prepare an approximately 0.05 *M* thiocyanogen solution according to Kaufmann's directions, using the utmost care in having all reagents and glassware absolutely dry. Wash approximately 0.2-gram samples of lard into 250-ml. glass-stoppered Erlenmeyer flasks with 20-ml. portions of anhydrous ether. Evaporate off the ether on a warm sand bath, removing all ether vapor with suction. Pipet 25 ml. of the thiocyanogen solution into each flask. (*Caution:* Do not use mouth on pipet.) Keep the flasks in a dark place for 17 hours. Add 20 ml. of a 15 per cent potassium iodide solution to each flask and at once titrate the liberated iodine with standard thiosulfate solution, using starch as an indicator. The thiosulfate solution is actually standardized in terms of iodine rather than in terms of thiocyanogen equivalents. Record the thiocyanogen number in terms of iodine number, as the iodine equivalent of the standard thiosulfate solution is known. Duplicate blanks should be run for each series of determinations.

EXPERIMENTAL RESULTS

Thiocyanogen and iodine numbers were determined on four samples of lard (a normal lard and three consecutive stages of hydrogenation of the same lard). These samples were furnished by the Research Laboratories of the Institute of American Meat Packers under whose auspices the work was done. The thiocyanogen and iodine numbers were calculated on the basis of the mixed fatty acids. From the data obtained were calculated the percentages of linolic acid, oleic plus iso-oleic acids, total saturated acids, and total unsaturated acids. These percentages are based on the total fatty acids and on the assumption that no acid of higher unsaturation is present (probably not strictly true, as traces of linolenic, arachadonic, and possibly other unsaturated acids are present). As both the iodine number and the thiocyanogen number of oleic and iso-oleic acids are 90, while the iodine number of linolic acid is 180 and the thiocyanogen number is 90, the following calculations may be made:

Per cent saturated acids = (90 − thiocyanogen no.) × 100/90
Per cent linolic acid = (iodine no. − thiocyanogen no.) × 100/90
Per cent unsaturated acids = 100 − % saturated acids
Per cent oleic acid = % unsaturated acids − % linolic acid

TABLE I. CHANGES IN LINOLIC AND OTHER ACID CONTENT OF LARD WITH PROGRESSIVE HYDROGENATION

LARD SAMPLE	IODINE NO. OF MIXED FATTY ACIDS	THIOCYANOGEN NO. OF MIXED FATTY ACIDS	DIFFERENCE (I − SCN)	OLEIC + ISO-OLEIC[a] ACID	LINOLIC ACID	UNSATURATED ACIDS	SATURATED ACIDS
				%	%	%	%
Original, not hydrogenated	65.5 65.3	54.9 54.8	10.6	49.1	11.8	60.9	39.1
Partially hydrogenated	61.4 61.5	54.8 54.5	6.8	53.1	7.6	60.7	39.3
Hydrogenated more than preceding sample	56.9 56.9	54.2 54.1	2.8	57.0	3.1	60.1	39.9
Hydrogenated more than preceding sample	51.0 51.1	50.1 49.9	1.1	54.4	1.2	55.6	44.4

[a] From partial reduction of linolic acid.

The results (Table I) show clearly that during the hydrogenation process one of the two double bonds of linolic acid is reduced almost completely before the reduction of the other double bond or of the double bond of oleic acid. The saturated fatty acids show no appreciable increase until practically all of the linolic acid has been reduced to an isomer of oleic acid.

The same thing has been shown by Barbour (*1*) for the hydrogenation of cottonseed oil. Barbour used 13 samples representing different stages in the hydrogenation and carried the hydrogenation nearly to completion.

Two similar series of determinations on lards in different stages of oxidation were conducted. The samples of lard were put in 100-ml. Erlenmeyer flasks and placed in an oven at 90° C. Air was continuously bubbled through the melted fat by means of a suction pump, in order that the oxidation might be uniform through the sample. Aliquots were removed for iodine and thiocyanogen number determinations at the end of 4, 7, and 15 hours. The results are shown in Table II.

TABLE II. CHANGES IN SATURATED AND UNSATURATED ACID CONTENT OF LARD SUBJECTED TO PROGRESSIVE OXIDATION

LARD SAMPLE No.	TIME OXIDIZED	IODINE No. OF MIXED FATTY ACIDS (Av.)	THIOCYANOGEN No. OF MIXED FATTY ACIDS (Av.)	DIFFERENCE (I − SCN)	ACIDS WITH ONE DOUBLE BOND[a]	LINOLIC ACID	UNSATURATED ACIDS	SATURATED ACIDS[b]
	Hours				%	%	%	%
12816	0	69.8	58.9	10.9	53.3	12.1	65.4	34.6
	4	70.3	59.7	10.6	54.5	11.8	66.3	33.7
	7	66.0	57.4	8.6	54.2	9.6	63.8	36.2
	15	58.9	53.1	5.8	52.6	6.4	59.0	41.0
12817	0	71.5	60.9	10.6	55.9	11.8	67.7	32.3
	4	69.8	60.8	9.0	57.6	10.0	67.6	32.4
	7	64.0	58.6	5.4	59.1	6.0	65.1	34.9
	15	52.0	51.2	0.8	56.0	0.9	56.9	43.1

[a] Includes oleic acid and the linolic acid having one of its double bonds oxidized.

[b] True saturated acids plus unsaturated acids with all double bonds oxidized.

From the data on hydrogenated lards (Table I) the following conclusions may be drawn: (1) A decrease of 1.3 per cent in total unsaturated fatty acids due to hydrogenation produces a decrease of 73.7 per cent in linolic acid content; (2) a decrease of 8.7 per cent in total unsaturated fatty acids produces a decrease of 90.0 per cent in linolic acid content.

From the data on the oxidation of lard (Table II, sample 12817) the following conclusions may be drawn: (1) A decrease of 3.8 per cent in total unsaturated fatty acids due to oxidation produces a decrease of 49.2 per cent in linolic acid content; (2) a decrease of 16.0 per cent in total unsaturated fatty acids produces a decrease of 92.4 per cent in linolic acid content.

It is evident that the linolic acid, or at least one of the double bonds of linolic acid, is much more reactive to both oxidation and reduction than is the double bond of oleic acid. As the linolic acid is oxidized first, the small amount of oxygen absorbed by a lard during its induction period must be due to the oxidation of linolic acid and possibly traces of more highly unsaturated acids. The rapid absorption of oxygen at the end of the induction period may be due to a catalytic effect exerted by the oxidation products of linolic acid. As the linolic acid may be mostly reduced by a very small amount of hydrogenation and as oxidation attacks the linolic acid first, it should be possible to greatly increase the stability of a lard by such a small amount of hydrogenation that the physical properties are not appreciably altered.

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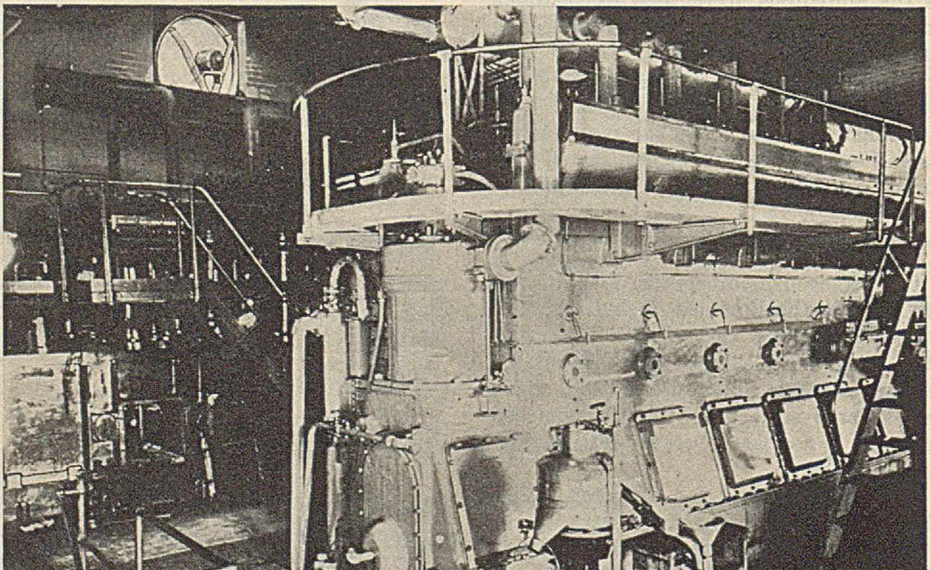

Courtesy Northwestern Fan and Power Co.

INTERIOR OF CITY WATER WORKS PLANT, MENASHA, WIS., VENTILATED WITH A PROPELLAIR

Indole and Skatole in Sewage

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IT IS well known that most of the odors observed around sewage-disposal plants are caused by sulfur compounds, mainly hydrogen sulfide and some mercaptans. Among the sulfides produced in the decomposition processes in digestion tanks, allyl sulfide, which has a penetration odor and occurs especially during the first stage of digestion, or when tanks are not performing normally owing to lack of sufficient seed material or acid conditions, is a striking example of an odor-producing substance other than hydrogen sulfide. There are, however, still other volatile substances which, diffused in extremely small quantities into the air, have a peculiar and penetrating odor. Two of these substances—namely, indole and skatole, which are nitrogenous degradation products—were selected for determination in three types of sewage-disposal plants. These substances, formed probably by a number of different bacteria in the processes of decomposition of proteins, are found in feces and may occur in spoiled fish, meat, and other nitrogenous food products.

The sewage plants selected were: Plainfield, N. J., consisting essentially of a fine screen, settling tanks, sprinkling filters, and digestors; Red Bank, N. J., with clarifier unit and digestors; and Madison-Chatham, N. J., with sedimentation and activated sludge.

METHODS USED

Considerable work was done to adapt methods suitable for the purpose. It was soon found that the quantities of indole and skatole present were very small.

INDOLE. A current of live steam was passed through the mixture in the flask until 500 cc. of distillate were collected. The steam from the flask was received from the condenser into an adapter, the end of which projected below the surface of a small amount of water in the receiver (600-cc. beaker). The distillate was transferred to a liter separatory funnel, acidified with 10 cc. C. P. concentrated hydrochloric acid, and extracted with 120 cc. ethyl ether (U. S. P.) with repeated and vigorous shaking of the funnel. After the ether had separated, the ether layer was transferred to a 250-cc. separatory funnel and washed free, first with 25 cc. sodium hydroxide solution (2.5 per cent), and then with 25 cc. dilute hydrochloric acid (10 cc. C. P. concentrated hydrochloric acid plus 200 cc. water). The first washing was to remove compounds which might interfere in the color tests, and the second to neutralize any alkali left in the ether. The ether was then placed in a small flask with 10 cc. of distilled water and evaporated on a steam bath, taking great care that, while the last of the ether was being driven off, the water layer was not heated appreciably above the boiling point of ether, since indole may be easily lost by volatilization at this stage. A 5-cc. portion of the 10 cc. of water residue was then tested for indole, and 5 cc. for skatole by the modified tests listed below.

SKATOLE. In the modified Ehrlich method the reagents used were (1) 2 grams of *p*-dimethylaminobenzaldehyde in 100 cc. of 95 per cent alcohol; (2) 600 cc. concentrated hydrochloric acid plus 200 cc. of water; and (3) U. S. P. chloroform. To 5 cc. of the water test solution 0.5 cc. of reagent 1 and 1 cc. of reagent 2 were added. This was placed in boiling-water bath for about 20 seconds, shaking vigorously, and then in ice water for about 30 seconds, and extracted with 1 cc. of reagent 3. Comparison was made with standards prepared in exactly the same way. The water test solutions consisted of 10 cc., which was equally divided into two thin-walled colorless glass test tubes, one used for the test and one held in reserve. The tubes were placed in a rack in numerical order; and a series of standard tubes containing 0, 0.5, 1.0, 1.5, 2.0, 3.0, 4.0, 5.0, and 6.0 mmg. indole in 5 cc. of water arranged in another rack. A series of reagent burets arranged on a revolving stand contained the following reagents: water, standard indole solution, *p*-dimethylaminobenzaldehyde solution, hydrochloric acid, chloroform, and sometimes a modified Herter's reagent and standard skatole solution.

RESULTS

The results obtained are summarized as averages of several tests in Table I. The quantities of indole and skatole in the raw sewage are small and seem to be about the same for the different places. These small quantities will produce a perceptible odor. It is of interest that the settled sewage in all cases contained less indole and skatole than the raw sewage. The rather stale Plainfield sewage contained more skatole than the sewage of the other two places. The effluents of the oxidation devices contained only traces of both indole and skatole. These volatile substances were either dispersed into the air or oxidized. The latter is more probably true than the former, since the odor arising from the aeration tanks is usually less than from a sprinkling filter, although all odors coming from sprinkling filters are by no means due to these nitrogenous compounds alone.

TABLE I. INDOLE AND SKATOLE IN DISPOSAL PLANTS

(Parts per billion)

PLANT	INDOLE	SKATOLE
Plainfield, N. J.:		
Screened sewage	0.25	0.38
Settling-tank effluent	0.12	0.25
Sprinkling-filter effluent	Trace	Trace
Red Bank, N. J.:		
Raw sewage	0.25	0.19
Clarifier effluent	0.12	0.12
Madison-Chatham, N. J.:		
Raw sewage	0.25	0.19
Settling-tank effluent	0.12	0.12
Aeration-tank effluent	Trace	Trace

The putrefactive processes producing indole and skatole proceed probably by deaminization, and it is possible that such odors can be controlled by alkalies or chlorine. This phase of the work has not, however, been carried far enough to determine the quantities of chemicals required.

SUMMARY

The nitrogenous degradation products, indole and skatole, which produce penetrating odors when diffused into the air, are present in raw sewage, to a less extent in settled sewage, and only in traces in sewage treated on sprinkling filters or by the activated sludge process.

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GRASSELLI MEDAL AWARD

LAWRENCE V. REDMAN, vice president and director of research of the Bakelite Corporation, and president-elect of the AMERICAN CHEMICAL SOCIETY was awarded the Grasselli Medal for 1931 on November 6 at the Chemists' Club, New York City, in recognition of his paper on "Cost of Research and Its Apportionment." An account of the accomplishments of the medalist in the field of chemical research was given by F. W. Willard as follows:

We in this land of snorting democracy and velvet-pawed oligarchy take ourselves too seriously. Not even our Mark Twains and Will Rogerses really succeed in making us laugh at our own inconsistencies. We have proclaimed and do annually or oftener reaffirm a political theory of individual equality, but our chief occupation is hero stalking. We cannot dramatize the group and its accomplishment, but must have a Hercules. No competent newspaper editor would dare try to feature on his front page the results of a group effort, no matter how extraordinary they might be. He would surely pick out one individual and pin it all on him.

Intellectual prowess is no exception. We just won't admit that great accomplishment is inherent in a group. We must have heroes in the science—Newtons, Faradays, Maxwells, Michelsons, Millikens, Einsteins, and Edisons.

Once in many long dogs' ages, a discriminating minority convenes and picks out of a virile functioning group of "fifth estaters" an individual, drags him out in front, and says to the world, "This fellow is no hero; all alone by himself he can't do much; but he made of himself a vicarious atonement for his associates, bore the drudgery of planning and coördination, settled disputes, gave them suggestions, got the money to pay them and to provide them with good tools, praised them when they succeeded, did not chide them when they failed, kept them on the main track, and gave them all the credit." Because Lawrence Redman has done these things, his associates have been able to create a great industry, making something which everybody uses every day, out of those vile-smelling twins, carbolic and formaldehyde.

Lawrence V. Redman is honored here tonight, not because he looks grimly down at us from the volumes of the *Journal of the American Chemical Society*, the *Berichte der deutschen chemischen Gesellschaft*, nor yet from the *Zeitschrift für angewandte Chemie*, but because he is one of a very few human catalysts who are synthesizing the applied sciences for the benefit of mankind.

Because of our feudal inhibitions we have been slow to admit the homogeneity of the physical sciences. Once admitted, progress in application to human needs can be obtained only by group research. It is being done even in our institutions of higher learning, those impregnable bulwarks of individualism. Industry, being painfully practical and profit-conscious, has adopted it without reservations.

I am sure that the commission of award did not go to Washington and minutely examine the 125 odd patents granted in the course of this phenomenal development of resinoids; perhaps they went over to Bloomfield and peeped in at the scores of research and development workers for whom the medalist is the coördinator. If they did, they probably didn't count them. Why should I recount these details, just because I can memorize a few figures?

The important fact is that, while Leo Baekeland by the judicious selection of catalysts developed a most useful material out of two very unpopular chemicals, he performed the act of supreme genius which revolutionized the electrical, mechanical, and decorative arts by staking his substance on group research catalyzed by Lawrence V. Redman. If there are any medals not working which have not already been given to him, they should forthwith be struck in Dr. Baekeland's honor for this act of vision and faith.

The Grasselli Medal is awarded annually by the American Section of the Society of Chemical Industry for the paper presented before that section which offers the most useful suggestion in applied chemistry. The previous awards have been as follows:

YEAR	MEDALIST	PAPER
1920	Allen Rogers	"Industrial Uses for the Shark and Porpoise"
1922	Walter H. Fulweiler	"Chemical Problems in the Gas Industry"
1924	B. D. Saklatwalla	"Ferrous Alloys Resistant to Corrosion"
1925	E. R. Berry	"The Manufacture and Uses of Clear Fused Quartz"
1926	Charles R. Downs	"Catalytic Oxidation of Organic Compounds in the Vapor Phase"
1928	H. J. Rose	"Importance of Coal Preparation in the Manufacture of Gas and Coke"
1929	Bradley Stoughton	"Light Structural Alloys"
1930	Per K. Frolich	"The Role of Catalysis in High-Pressure Reactions"

Research as a Fixed Charge

LAWRENCE V. REDMAN, *Bakelite Corporation, Bloomfield, N. J.*

IN EVERY well-conducted business there are certain charges that have long been considered as inescapable. Included in these are interest on borrowed capital, rents, taxes, insurance, depreciation, obsolescence. It is time, in this industrial age, that there be added to these fixed charges a charge for an adequate and sustained program of research without which no industry can progress, if indeed it can survive.

We are in a changing world. New and better things, new and better methods, are continually supplanting the old. This was recognized when obsolescence became a fixed charge against equipment. Although the accountant may never have thought of this as a charge for research, it is in no small measure indirectly just that. Since progress thus assesses a tax against industry, self-interest suggests offsetting this tax by the profits that accrue to invention.

Our more progressive industries are endeavoring to maintain a consistent research program, but constant sustained research has not yet acquired the status of an obligation of sound management in the minds of many of those who are in control of business finance. Too often in the past has research been thought of as a luxury to be indulged in during a period of large profits and renounced when dividends could no longer be fully maintained. Better might a manufacturer cancel his fire insurance than drop his only insurance against retrogression.

Nor can the manufacturer hope to profit, even if he would, through bringing unnecessary hardship on his men of research, whose success, not to say livelihood, is, like his, dependent upon sustained research effort. But while it is these who are mainly affected, everyone is the loser through wasteful interruption of research. It is encouraging to note the growing tendency at our universities to endow research as well as instruction so that new knowledge in pure science, the very foundation of modern civilization may continue to grow, affected little or not at all by the ups and downs of the commercial world. It is encouraging also to note that our Government for many years has accepted as a permanent charge the cost of research in certain of its departments—notably in agriculture, standardization, the navy, the army.

Gradually we in industry are realizing that research is a necessity for good times and for bad alike; a necessity in good times to provide full employment for willing capital and greater return for labor; a necessity in bad times to prepare for the good times that are to follow. Also, as has been recently so well set forth by C. F. Kettering, it is a necessity in bad times if we are to tempt forth from hiding the reluctant hoarded dollar. It is an accepted, if somewhat new tenet of the economist, that not only is there at all times a saturation point in the consumption of necessities, but, when the nation is saving, it is only the new things, not the commonplace, that tempt hoarded money from its hiding. There is indeed wisdom on the side of the management that feeds out the results of successful research and development at a rate that will insure reasonable continuity of output. There is added wisdom in seeing to it that not the least attractive of the new things are those scheduled to appear during times like the present. Is it not since this period of depression started, and in spite of it, that Cellophane has burst upon us?

Lawrence V. Redman

Slowness of Research

But success in research and development comes on the average only after a long pull. True, we sometimes realize handsomely after only small expenditure of time and money. These bits of good fortune, however, serve merely to offset those adventures that prove to be dead losses. If we would prosper through research and development, we must count on years of outlay of money and effort; or make no start at all. Average experience suggests as a fair expectancy, from the start of research to full liquidation of the investment, a period of seven or eight years. If this time seems too long to the average investor, we would remind him that certain engineering projects call for an equal exercise of patience. Keynes in his "Treatise on Money" tells us that in gold mining an average of about seven years is to be expected before the beginning of returns, when the sinking of the first shafts, the building of crushing mills, etc., are taken into consideration. There should be no complaint if our speed of return of capital from investment in research is equal to that of successful gold mining. A glance at the time required for planning and building our new tunnels and bridges would indicate that before returns are adequate, capital so invested requires as long a pull as does that invested in average research.

I know there is no one within the hearing of my voice who is not fully mindful of the existence of this long-time factor. We are anxious that the same may be said of our business executives the country over. We believe that among our leaders in business and industry the number is diminishing of those to whom science is synonymous with mystery and to whom its creative processes are lucky whirls of the wheel of fortune, or are instantaneous discoveries, instead of coming only as the result of sustained exercise of scientific skill. Recently one of our professors of philosophy has said that the great discovery of the nineteenth century was the method of discovery. It is for the sustained application of the method of discovery that we are pleading.

Research will never be oversold to business. But it may be wrongly sold, and, if there is one danger greater than another in any statement of the possibilities of research, it is that the time factor will be too lightly stressed. Who has not had occasion to view with dismay the enthusiasm of a proponent who would have his associates risk a fortune on a test-tube experiment, or the scarcely less foolhardy who would plunge into advertising on the appearance of the first hundred pounds successfully made. Such acts make investors the prey of the overenthusiastic, the injudicious, and sometimes the unscrupulous, whose glowing promises of success are alluring even when heavily discounted. On the other hand, who of you has not felt depressed and broken in spirit from being advised, even urged by a financial associate to stop some project which there is every reason to believe will be profitable if only time is allowed to bring it to completion. It is generally your pet project, too remote and profound, shall I say, to be understood or believed in by the uninitiated.

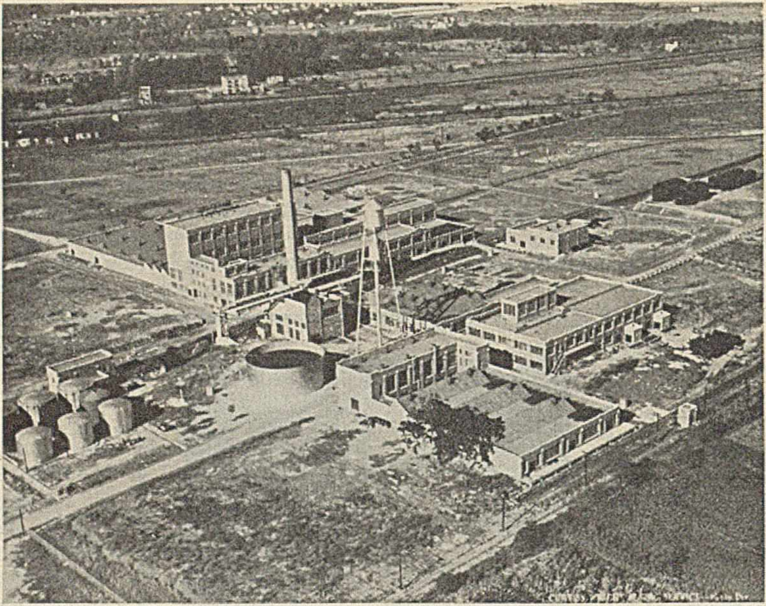
Necessity for Continuous Effort

Organized research is too new for the laws governing its successful prosecution to be well understood by the business world. Chemical processes are not as easily visualized as engineering plans. The route from test tube to factory equipment is flanked by greater dangers than that from blue print to structure. It is for us who know the limitations as well as the possibilities of research not only to maintain and instil into our financial associates courageous enthusiasm in the face of difficulties, but also to give early warning that, to be successful, a promising project once launched into development must be prosecuted through the years of discouragement, sometimes at heavy cost of money and nerves.

To make continuity of effort possible, the program of research and its much more expensive development should be held to an even keel. It must not be overdone in a period of prosperity if it is to be maintained in a period of depression. Is it too much to hope that the practice of putting by a surplus fund for research when there is enough and to spare, to be drawn on when retrenchment is the order of the day, will soon become a commonplace of sound industrial management? Men put aside surpluses that dividends may be continued uninterruptedly. Why not surpluses that the production of new knowledge may be consistently maintained?

There have been many methods of financing research in the past. Companies have been formed whose subscribed capital was consumed in research, as was the case with Thomas Edison's invention of the electric light. We have had the more arduous method such as Alexander Graham Bell used when entertainments and theatrical shows were given by himself and Watson, and the gate receipts used to defray the expenses of carrying on his telephone research. All too often there has been no adequate financing. The privations of genius took the place of sane financing. Goodyear carried on his research in the vulcanization of rubber while he was in jail over in Philadelphia as a common debtor.

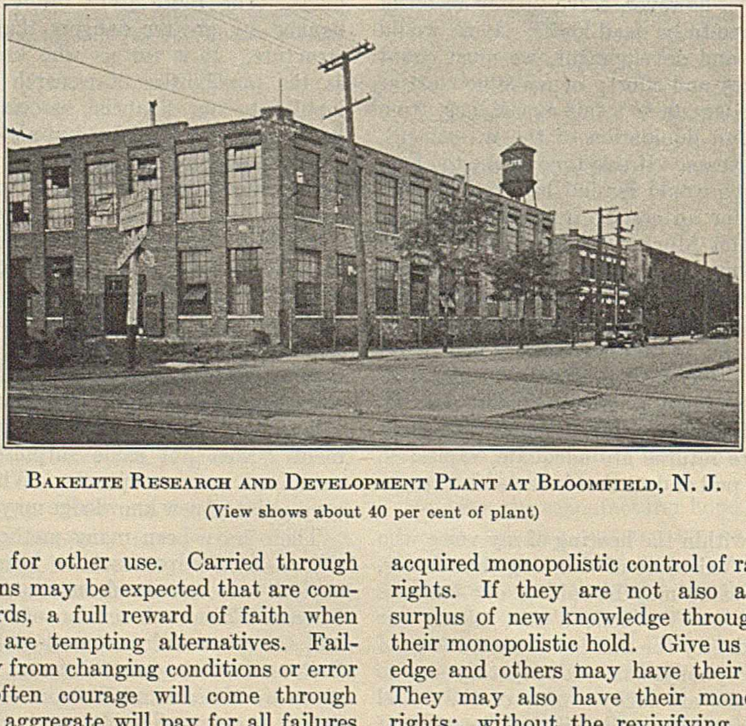
We are vastly indebted to these undaunted individual researchers who at great personal sacrifice struggled on to success often with piteously inadequate backing. We confidently expect future generations will proclaim their indebtedness to modern organized research which has already abundantly justified itself in dividends to its sponsors and much greater dividends to mankind. In a broad program of sustained well-conducted research, the successes may be depended on to more than offset the failures. It is in accordance with the whole past history of invention. As in insurance, multiplying the number of hazards enhances the safety of prediction. If we consider the aggregate of individual researches, the balance is overwhelmingly on the side of the successes. We need cite only the achievements named above to justify all of the money expenditure and personal sacrifice of all of the inventors of all time. With every reason for confidence in the ultimate success of a broad sustained program of research, we are urging that the reward be not lessened, be not lost, through the inefficiency of discontinuous effort.



Airplane View of Bound Brook Plant of Bakelite Corporation

Dangers to Be Avoided

There are certain dangers that beset us in such a program of research. Perhaps the greatest is that from overexpansion in the development period and its overdemand on available capital. A development project abandoned before it is demonstrated to be a commercial success becomes almost a total loss, for the equipment is ordinarily of a special character and of little or no value for other use. Carried through to success, however, returns may be expected that are commensurate with the hazards, a full reward of faith when doubt and abandonment are tempting alternatives. Failure is always a possibility from changing conditions or error of judgment, but more often courage will come through with successes that in the aggregate will pay for all failures with a handsome margin.



Bakelite Research and Development Plant at Bloomfield, N. J.

(View shows about 40 per cent of plant)

When there are many promising development projects coming out of research, only the most promising may be started in development even in the best of times, and then only at suitable intervals if the situation is not to get out of hand. We are speaking of course about major development projects arising from research. The preliminary small-scale work or research proper is not self-limiting to any such degree. Such work wisely directed is relatively inexpensive and should pay its own way in terms of new knowledge. There will naturally be a considerable number of research problems under study for everyone that shows enough promise to warrant being put into development. It is the promising, the successful, research that tempts us into financial difficulties. When the funds are not forthcoming for launching even promising development projects, research basic to the industry may well occupy the time of the trained personnel, for, when confidence is again restored and promising development can be financed, it should be possible to profit greatly from the new knowledge gained.

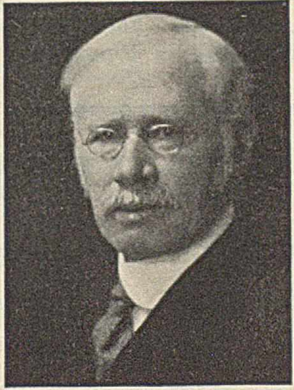
A surplus of new knowledge, new ideas, new intellectual property, is a real asset, more real in determining industrial leadership than are raw materials or, in the long run, than patent rights. New knowledge is tomorrow's inventory of greatest value. When we lay aside knowledge, ideas, plans against the future, we speak of pigeonholing them. Such intellectual property has not acquired the status of an asset in today's bookkeeping. Perhaps sound financing would dictate that it never should, but it will surely appear in tomorrow's achievements. Many future successes lie dormant in today's unused new knowledge. Men have acquired monopolistic control of raw materials and of patent rights. If they are not also acquiring a commensurate surplus of new knowledge through research, they will lose their monopolistic hold. Give us a monopoly of new knowledge and others may have their corners in raw materials. They may also have their monopolies of existing patent rights; without the revivifying, the revolutionizing power of research, their advantage will be short lived.

Throughout the world today doubt and uncertainty have taken possession of men generally. Confidence in the future appears to have declined with the market for securities. This is a time calling for faith in the ultimate triumph of research's creative processes, challenged by those, like Gandhi, who would have us return to the primitive, scolded by those who would have us believe that an admittedly faulty division of wealth is the source of all our troubles. We confidently believe that creative science, producing for all enough and to spare, is the necessary first step away from poverty. Ours is the privilege of profiting a little while we add vastly more to the wealth of all. We shall succeed in proportion as our creative program is not intermittent and wasteful but is sustained and efficient.

EDITOR'S NOTE: Dr. Redman, in receiving the medal, emphasized that he accepted it as a token of approval of the work done by the corps of scientific men of his organization, and as an evidence of approval of the ideals inherited by them from the founder of their industry.

AMERICAN CONTEMPORARIES

Edward Kremers



THOSE Wisconsin University students who have spent even so little as an evening with Edward Kremers at his delightful retreat at "Highlands" on Mendota's lovely hills, or at his earlier home on Wingra's quiet shores, have learned to love the master even as they had first learned perhaps to fear him and then revere him. The undergraduate became the devoted disciple in his graduate years, as in these delightful gatherings Dr. Kremers' enthusiasm and devotion to science were imparted with inspiration to his student guests; his lectures at the University were replete with the learning of alchemist, sage, and scientist, and crowded with facts, but these quiet social hours revealed the true greatness and heart of the man and are counted among the treasured hours of memory by hundreds of his old students. As an admiring alumnus aptly put it, "Many have come to him to learn the art of making pills and have departed as doctors of philosophy."

Dr. Kremers, professor of pharmaceutical chemistry and director of the course in pharmacy at the University of Wisconsin, was born in Milwaukee, Wis., on February 23, 1865. He has throughout his life remained a loyal citizen of Wisconsin and married a Wisconsin girl, the present Mrs. Kremers, who has been a loyal helpmate throughout his active career and who is no less beloved by his students than he is himself. For only two short periods did he reside on other than Wisconsin soil—once in 1884 while attending the Philadelphia College of Pharmacy in his junior year after serving an apprenticeship in pharmacy in Milwaukee, and again in 1888–90 while studying abroad. From Philadelphia he returned to Wisconsin to complete his undergraduate work at the university where he graduated in 1888. Under the genial leadership of the late F. B. Power, he began his researches on volatile oils and photochemistry which have brought fame and honor to him among the scientists of the world. This inspirational influence led him to leave Wisconsin temporarily a second time to study under the illustrious Wallach, at Bonn University, who was then the outstanding authority in the field of terpene chemistry. When Wallach left Bonn, Kremers in company with other students, as was the custom of those days when men went to great teachers rather than to rich universities, followed the master to Göttingen, where in 1890 he took the Ph.D. degree at that university with a dissertation on the isomerism within the terpene group which was the foundation for many a research in the following years. On Dr. Power's invitation he returned to the University of Wisconsin to accept a position on the staff of the School of Pharmacy, and, when Power left to become director of the Wellcome Research Laboratories in England, Kremers became his successor, beginning therewith a long series of years of faithful service to the university and to the state. In the rise of Wisconsin from a small state university to its enviable position of greatness among America's foremost institutions of learning, Dr. Kremers has played no unimportant part. He established the first graduate work in America leading to the degree of doctor of philosophy for research in plant chemistry or pharmacy. Each year since he has had at least a dozen graduate students in lecture room and laboratory who have come from all parts of the United States, and some who have come from foreign countries.

He is a wise and helpful counselor to many a friend and student, always considerate of their best interests. Many owe to him the support for the continuance of their research work and studies, for, with untiring energy and often the hardest work, he secured for his research assistants scholarships or fellowships even in those early days when university and commercial fellowships were far less common than they are today, sometimes by minor subsidies or by loans, encouraging them in travel to attend meetings of scientific societies in the interest of their research and their development.

Dr. Kremers is fond of music, that is, good music of the classic variety, but on occasion also indulges in song, especially the songs of good fellowship of his own student days in Germany, and is also quite human in that he enjoys a good game of cards and a good joke. But these events occur only now and then, for Dr. Kremers is an indefatigable worker and every working hour of the twenty-four is put to some serious task in the acquiring and giving of knowledge. He is devoted to his books and is quite a bibliophile, possessing many rare old volumes of medieval medical, pharmaceutical, and alchemical science and history. One of his hobbies has been to collect old books and apparatus, bottles, cans, mortars, pestles, counters, scales, and the like, remnants of an age that is past or passing, in order to reconstruct an exhibit of the early days of pharmacy in the United States which as the "Old Apothecary Shop" is now one of the treasured exhibits of the Wisconsin Historical Library.

He was historian of the American Pharmaceutical Association for many years and has contributed many articles on the history of chemistry and of pharmacy; he is an honorary member of the Societé d' Histoire de la Pharmacie of France.

As a devoted lover of nature he works in the quiet retreat of his home acres and practices gardening and horticulture with rare skill. A rock garden with flowers and plants of many lands was receiving his especial care on the occasion of my last visit, and his enthusiasm here was just as great as over some intricate problem of the constitution of the then recently isolated hydrocarbon, azulene. His intersts and activities have not been entirely along purely academic lines. He recognized the value of actual contact with the living plant in the teaching of pharmacognosy and thus conceived and started the first pharmaceutical experiment station, whereby the medicinal plant garden was made an adjunct to the textbook and lecture room. Thus also the production of better vegetable drugs was emphasized and demonstrated. This experimental garden of medicinal plants at the University of Wisconsin is unique and well worth a visit. Through his efforts, practical pharmacognosy has found a permanent place in the pharmaceutical curriculum.

Of Dr. Kremers' preëminence in organic chemistry I need not speak, as this fact is well known to all readers of these pages. His contributions to chemistry have been numerous and varied. His work in the field of the volatile oils has been enormous and will forever associate his name with the development of this science and this industry. He has been a member of the Revision Committee of the United States Pharmacopeia and chairman of the subcommittee on volatile oils, and has issued an English translation of Gildemeister and Hoffmann's exhaustive work on volatile oils. He was twice awarded the Ebert Prize for his researches in this field, once in 1887 and again in 1900.

Two circumstances indicate the high esteem and appreciation in which Dr. Kremers' work and personality are held by his fellow scientists, colleagues, and students. When recently Dr. Power, who finally returned to the United States to engage in phytochemical research in the Bureau of Chemistry and Soils, died suddenly without writing his contemplated monograph on phytochemistry, scientific friends and former students of Dr. Kremers turned at once to him as the outstanding authority to write such a treatise, petitioning the university authorities to relieve him temporarily of administrative and professorial duties that he might the more speedily set down from his rich store of knowledge the vital facts of phytochemistry for future students and investigators in this field. The other instance lies in the fact that through former students a fund has been subscribed for a portrait of Edward Kremers, which is now being painted by a noted artist and is soon to be presented to the University to adorn its halls and hang, no doubt, alongside the portrait of his friend and associate, Dr. Power, as a tribute from those who loved well the man, revered the investigator, and honored the teacher.

OSWALD SCHREINER

BOOK REVIEWS

ANALYSIS OF LEATHER AND MATERIALS USED IN MAKING IT. *By John Arthur Wilson and Henry Baldwin Merrill.* 512 pages. McGraw-Hill Book Company, Inc., New York, 1931. Price, $7.00.

THIS book is a compilation of various methods for the analysis and testing of leather and the more important materials which go into its manufacture. The authors discuss the principles of the various tools which are employed in the leather industry. It is pointed out that most of the analytical methods used in this industry are purely empirical, and that the results from these empirical methods may be used to absurdity in the hands of one who does not know their limitations. In pointing out these various limitations, the book serves as a helpful guide.

The work is quite comprehensive, beginning with the analysis of the skin, and gives the standard empirical methods of testing skin and leather. All through the book much space is given to describing the mechanical equipment which the leather chemist employs; for example, in the chapter, "Microscopic Examination of Skin and Leather," the principles of a microscope are described at some length. The chapters on bacteria counts and enzyme activities are dealt with very gingerly, the authors perhaps being not so sure of their ground on this very important realm of leather chemistry. Chapter 7, "Measuring the pH Value," is one of the best in the book. It discusses in an elemental way the technic required for precise pH measurement, briefly describes the principle of hydrogen-ion concentrations, and gives detailed information on the calomel electrodes, quinhydrone electrodes, and the principle of the potentiometer in measuring the voltage of the cell. Colorimetric methods are also discussed. Chapter 8, entitled "Beamhouse Materials and Lacquers," reads very much like a laboratory manual on quantitative analysis. The methods of analyzing water and various inorganic salts are given in minute detail with formulas for calculations. In Chapter 9 on "Vegetable Tanning Materials," the authors reprint the A. L. C. A. hide-powder method of determining vegetable tan materials, and also the Wilson and Kearn method, and discuss the merits of the two methods. Chapters 10 on "Chrome Tanning," 11 on "Fat Liquoring and Stuffing Materials and Liquors," and 12 on "Coloring, Finishing, and Miscellaneous Materials" follow the same detailed style. There is added, for good measure, the last chapter on the preparation of standard solutions giving the elementary details found in any textbook on inorganic chemistry.

The book is well illustrated and the bibliography contains about 600 citations. The authors usually give the accepted A. L. C. A. method for the analysis in question and then follow with methods which have been developed by the authors or their co-workers. This book should be very valuable in a leather chemist's hands, as it places in one volume the information which he would have to glean from many references.

CHAS. ALLEN THOMAS

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RECENT ADVANCES IN ANALYTICAL CHEMISTRY. VOLUME II, INORGANIC CHEMISTRY. *By C. Ainsworth Mitchell and Contributors.* 452 pages. P. Blakiston's Son & Company, Inc., Philadelphia, 1931. Price, $3.50.

CHEMISTS will be grateful to the authors for this admirable book which has been anticipated since the publication of the first volume under the editorship of Doctor Mitchell. The reviews and abstracts are arranged in sixteen chapters, covering Hydrogen-Ion Concentration; Lead, Bismuth; Mercury, Copper; Cadmium; Arsenic, Antimony, Tin; Selenium and Tellurium; Platinum and Its Congeners; Iron, Chromium; Aluminium; Beryllium; Constituents of Steel; Carbon, Manganese, Aluminium, Molybdenum, Phosphorus; Nickel, Chromium, Cobalt, Arsenic, Tantalum, Uranium, Copper, Tin, Sulfur; Silicon, Cerium, Zirconium, Tungsten, Titanium, Vanadium; Gases; Carbon: Graphites and Carbon Blacks; Silicon; Cerium and the Rare Earth Metals: Scandium, Gallium, Indium, Thallium; Titanium, Zirconium (Hafnium), Thorium, Germanium; Vanadium, Niobium and Tantalum; Cobalt and Nickel; Manganese and Zinc; Molybdenum, Tungsten, Uranium; Magnesium; the Rarer Alkali Metals: Lithium, Rubidium, Caesium; Microchemistry; Water and Sewage Analysis. The reviewer is impressed by the evident care that is shown in balancing the treatment of subjects; in numerous instances sufficient details are given for carrying through procedures without further reference to the original literature. Verification of more than a hundred references taken at random indicates the accuracy of the reference work.

The publishers have done a good job too in their coöperation by reproducing sketches of apparatus, which is particularly noteworthy under treatment of microanalytical and electrometric methods. Eighty pages are devoted to micromethods, under a general survey of processes and materials, followed under physical processes by lengthy sections on spectroscopic, physico-chemical, radiometric, electrolytic, electrometric, nephelometry, liquid striation, fluorescence, luminescence methods; microchemical methods are presented under inorganic and organic, with distinct separation of qualitative and quantitative methods. A valuable table is given in this connection, too, of "Organic Reagents in Inorganic Qualitative Analysis."

A chapter of 53 pages on "Water and Sewage Analysis" is well worth the total cost of the book. No doubt is left as to the necessity of the sanitary engineer becoming familiar with organic, biological, and bacteriological methods, as well as purely mechanical processes. The reviews of progress in this field should elicit much attention.

It is not enough to state that the book should be in every general or departmental library. Chemists in the industries and teachers should have easv access to the volume.

Friend E. Clark

* * *

COLLOIDS. *By Ernest S. Hedges.* 272 pages. Longmans, Green and Co., London, New York, 1931. Price, $4.50.

This is a very modern book in spite of something more than a lack of emphasis on recent American research. The author may be pardoned a very human inclination to ride his own hobbies rather hard.

On pages 39–44 the author presents an excellent explanation of the Brownian movement, including the colloidal atmosphere of Perrin. Just as excellent is the section, pages 58–66, dealing with the origin of the charge. In this section adsorbed ions are well considered.

The chapter on emulsions, however, is very short and very poorly done. Evidently the author has done more research on reactions in gels than on emulsions. The reviewer was frankly disappointed with the section on adsorption and with the failure to discuss adequately the colloidal functions of porous charcoal, silica gel, activated alumina, etc. Dialysis, on page 72, fails to include the use of cellophane sausage skins. We are still waiting for a good chapter on organosols, a chapter in great need of development.

Sensitization on page 109 is very clearly discussed and shows the author at his best. The term "tactosols," coined in 1929 for an old phenomenon, is frankly adopted. To be quite up to date and meticulously correct, the author should use the general term "electrophoresis" instead of the one-way phrase "cataphoresis." However, very few authors have dealt with these terms correctly. Hedges is in advance of most writers in using the term "electro-osmosis" although the reviewer prefers "electric-osmose." Considering that both endosmosis and exosmosis have been observed, it is painful to hear so many scholars use only the term endosmosis. Our newest book on colloids should have discarded the incorrect representation of a millimicron by $\mu\mu$. As shown in Vol. II of the International Critical Tables, the correct representation is $m\mu$. It is interesting to note the use of the phrase "lyosorption" for negative adsorption.

There are many excellent things in this book, and it is well worth reading. For example, on page 20 there is a stimulating statement about the lattice blocks in crystals. There is nothing hackneyed in the treatment of the subject, for, on the contrary, a great deal of fresh vigor has been put into the writing. We welcome the book as a useful addition to any library.

Harry N. Holmes

* * *

NUCLEIC ACIDS. *By P. A. Levene and Lawrence W. Bass.* A. C. S. Monograph No. 56. 337 pages, 14 × 22 cm. Chemical Catalog Company, Inc., New York, 1931. Price, $4.50.

This is an excellent summary of the chemistry of nucleic acids constructed in accordance with the historical method of discussion. The authors have presented their review in a very complete manner and have incorporated many literature references which will be of great service to future workers in this field. They acknowledge in their preface the value to them of the two excellent previous monographs on "Nucleic Acids" by Professor Walter Jones of Johns Hopkins University in English, and the German monograph by Professor R. Feulgen, and have reviewed with thoroughness the theories and results of experimental work which have finally led up to the present development in this specialized field.

Of the 337 pages, all but 30 are devoted to a discussion of the chemistry of nucleic acids. The subject matter is presented in two sections. Part I deals with the components of nucleic acids, and is subdivided into 7 chapters covering the following subjects: sugars, imidines, imido esters and imidazoles, pyrimidines, uric acid and purines, purine bases, and nucleosides and nucleotides. It is important to mention that the senior author and his coworkers have contributed a large proportion of the experimental work discussed, which has led up to our present conception of nucleic acid composition. These developments represent one of the most interesting chapters in our newer knowledge of cellular chemistry.

In Part II are discussed the more general and historical aspects of the subject matter, including chapters dealing with the discovery of nucleic acids and of their components, structure, nucleic acids of the higher order, and the nucleases, and properties of the individual enzymes which are capable of reducing the nucleic acids to simpler combinations.

The wide experience of the senior author in this field of biochemistry has made possible a comprehensive and coördinated review which will be recognized as a valuable scientific summary of our present-day information in this field of cell chemistry. The book will be received with great interest by every worker in biochemistry, and will serve as a guide to all future work in the further study of nucleic acid chemistry. No library of biochemistry would be complete today without the incorporation of this useful monograph.

Treat B. Johnson

* * *

PHOTOCHEMICAL PROCESSES: A GENERAL DISCUSSION. Reprinted from the Transactions of the Faraday Society. 216 pages. Gurney and Jackson, 33 Paternoster Row, London, E. C. 4, April, 1931. Price, 10 s. 6 d.

The fifty-fifth "general discussion" organized by the Faraday Society was held at the University of Liverpool on April 17 and 18, 1931. The program was devoted to a consideration of photochemical processes. It was divided for the purpose of grouping related papers into four major divisions: (I) molecular spectra in relation to photochemical change; (II) photochemical kinetics in gaseous systems; (III) photochemical change in liquid and solid systems; and (IV) photosynthesis. Each group of papers is preceded by an introductory paper or address (Mecke, Bodenstein, Berthoud, and Baly) which serves as a foundation for the papers and discussions which follow. Most of the twenty-three papers comprising the four groups elicited general discussions (sixteen in all), and these discussions frequently served to bring out very diverse points of view. The advantages of such general discussions, or symposia, are now well recognized. Students and investigators in the highly specialized field of photochemistry will find this particular group of papers invaluable.

J. H. Mathews

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THE STRUCTURE OF CRYSTALS. *By Ralph W. G. Wyckoff.* 2nd edition. A. C. S. Monograph No. 19. 497 pages. Chemical Catalog Company, Inc., New York, 1931. Price, $7.50.

The important developments in the field of crystal structure since 1923 have made it necessary for the author to rewrite this book completely from a somewhat different viewpoint from that of the first edition. In the first 200 pages an account is given of the properties of x-rays and crystals and of their interaction, followed by a discussion of the methods of determining the structure of crystals. The mathematical treatment is not made unduly difficult by the introduction of rigorous and general proofs, and the discussion should be especially useful to chemists and experimental physicists who desire to carry on work in this field. Sizes of ions and atoms and other subsidiary aids in structure determinations are also discussed. The next 200 pages contain an account of individual structures. A laudable critical attitude has been maintained, full descriptions with drawings being given of all published structures which have a high probability of being correct, even when auxiliary information such as ionic radii has been used in their determination. Suggested structures which have not been satisfactorily substantiated are mentioned but not described in detail. The drawings are mostly clear, the packing drawings in which atoms and ions are shown as spheres in contact being especially instructive. For complicated structures reference to the drawings in the Strukturbericht of Ewald and Hermann to supplement those given by Wyckoff is to be recommended. The book ends with a 75-page bibliography of crystal-structure data, listing nearly 3000 references, and a subject index.

The monograph provides a readable and authoritative account of the methods and results of crystal-structure investigation at the present time, and can be recommended to any chemist who wishes to obtain more than a superficial acquaintance with this field. Linus Pauling

THE CHEMISTRY OF FLAVOURING AND MANUFACTURE OF CHOCOLATE, CONFECTIONERY, AND COCOA. *By H. R. Jensen.* 406 pages, 23 illustrations. P. Blakiston's Son & Company, Inc., Philadelphia, 1931. Price, $7.50.

This book is of decided interest to the technician employed in the chocolate and confectionery industry. More than half of the volume is given over to the consideration of cacao, chocolate, cocoa powder, and confectionery fats. The remainder of this treatise deals with sugar, milk, colloidal agents, flavors, colors, analytical notes, and recognized standards. Of especial interest is the manner in which the author points out definitely the function of the chemical laboratory and limitations imposed on it through insufficient coöperation. The frankness with which he treats his subject is aptly illustrated by the closing paragraph of his introduction where he states: "The chemist too often alone understands how his work is to be made effective, and, in short, he needs to be treated as a vital productive as well as a protective unit."

Jensen, through his connection as former Chairman of the Consultative Panel, British Research Association for Cocoa and Chocolate, is ably fitted to handle a treatise of this nature. His discussion of cacao varieties, their botanical origin, handling, normal variation, methods of grading, and general acceptability is decidedly instructive. Composition of different types of cocoa and chocolate and their physiological properties, as well as methods of manufacture and efficiency of equipment, are discussed in detail. A review of materials other than chocolate and cocoa makes of this book as complete a treatise as is possible in the limited space at the author's disposal.

The book will be a valuable addition to the library of all food manufacturers, and, while written largely from the standpoint of the technician, it will be of interest to the executive, since it deals with vital factors in such a comprehensive manner that information contained makes of it an indispensable reference book. Stroud Jordan

WAVELENGTH TABLES FOR SPECTRUM ANALYSIS. *Compiled by F. Twyman and D. M. Smith.* 2nd edition. xi + 180 pages, 3 figures. Adam Hilger, Ltd., London, 1931. Price, 14 s. 6 d.

Much new material has been included in this revision of the book originally compiled by the senior author alone. The tables of standard wave lengths have been enlarged to include the International Astronomical Union's 1928 recommendations, as well as other recent precision measurements in the spectra of iron and the inert gases. The tables of distinctive lines, determined by Hartley, Pollok, Leonard, and Whelan, have been converted to international units, making them more readily comparable with recent work.

One chapter from the earlier edition has been omitted, and four new ones added. These include one on the various types of spectra, contributed by Professor Andrade, and one on the sensitive arc lines of 50 elements, a welcome addition since most published tables deal only with the spark. A short chapter gives tables of sensitive lines in flame spectra, and there is a general summary of the most persistent lines of some sixty elements in both the arc and spark, as observed by a number of authorities. De Gramont's table of "Raies de grande sensibilité et raies ultimes" remains as in the previous edition with minor corrections and a few additions.

An error that has crept into at least three other compilations of spectrum tables in the last few years is repeated in this one. In Parts V and VII the wave lengths given for phosphorus are in error, being vacuum values, whereas those of all the other elements are for atmospheric conditions. Each should be corrected by subtracting 0.76 Å. De Gramont's table in Part IV-B gives them correctly.

Spectral analysts will find this a very convenient reference book, although it hardly fulfils the ambition outlined in the preface, "to supply a book...so complete that reference to other sources of information would rarely be necessary." Charles C. Nitchie

LINOLEUM HANDBUCH. EIN PRAKTISCHER FÜHRER FÜR INDUSTRIE UND HANDEL. *By H. G. Bodenbender.* 506 pages. Illustrated. Chemisch-technischer Verlag Dr. Bodenbender, Berlin-Steglitz, Germany, 1931. Price, 12 marks.

This is an excellent work in which various types of linoleum are illustrated in color and which includes in addition to statistics a very thorough discussion of raw materials of manufacture, formulas, and similar details. A considerable section of the book is devoted to plant equipment employed in the manufacture of this floor covering, plant lay-out, and processes. There is a section giving tables of data with special reference to the linoleum industry, another section abstracting patents, and another giving details of various concerns throughout the world engaged in linoleum and floor-cloth manufacture. This includes lists of plants with their officials, boards of directors, branch offices, and financial statistics. Trade associations are discussed and world statistics given. In addition to all this, there is a discussion of the proper use and application of the material and a number of pages devoted to definition of terms peculiar to the industry. The volume is well indexed, and all in all offers a work of considerable value to the industry, its several branches, and those who for any reason may be interested in the subject.

KOLLOIDCHEMIE DES GLASES. *By Ralph Ed. Liesegang.* 49 pages, 12 figures. Theodor Steinkopff, Dresden, 1931. Price, 4 marks.

The title covers the section on Glass of the second revised edition of "Kolloidchemische Technologie" which is being edited by R. E. Liesegang, and includes thirty-seven additional sections.

The glass portion is divided as follows: I. Nature of Glass; II. Particle Size of the Raw Materials and in the Melt; III. Cooling and Hardening; IV. Devitrification; V. Opal and Alabaster Glasses; VI. Etching and Polishing; VII. Cracking and Cutting of Glass; VIII. Color Production; IX. Viscosity; and X. Gases and Water in Glass.

Under "Nature of Glass," the colloid-electrolyte theory is discussed with the older controversial material. In Chapter IV, Liesegang naturally devotes considerable time to ring formations during devitrification, and also discusses x-ray studies. Chapter V includes methods for direct chemical production of opalescence as well as through ordinary agents in normal glasses. This chapter is illustrated with photomicrographs of crystal- and colloid-forming substances. Chapter VI is concerned with studies of surface etching with the microscope, and illustrates various effects produced. In Chapter VIII, particle size and conditions for coloring agents such as silver, copper, selenium, tellurium, sulfur, and charcoal are included. In Chapter IX, the important subject of viscosity control is elaborated. The last chapter tells of naturally occurring gases and water in glass, and of adsorption and absorption tendencies. Color adsorption is included in this discussion.

This section of Liesegang's revision of "Kolloidchemische Technologie" is an important contribution to the science of glass-making and the study of the finished product. It includes the most up-to-date journal references from Holland, England, America, Germany, France, Japan, Italy, and Russia by leading authorities. A. Silverman

CHEMISCHE UNTERSUCHUNG DER SPRENG- UND ZÜNDSTOFFE, UNTER BESONDERER BERÜCKSICHTIGUNG DER ZU IHRER HERSTELLUNG NOTWENDIGEN AUSGANGSSTOFFE. *By Ludwig Metz.* Based on manuscript left by Hermann Kast. 583 pages. Friedr. Vieweg & Sohn, A.-G., Braunschweig, 1931. Price, paper, 40 marks; bound, 42.80 marks.

Every important explosive, every important priming agent, and every raw or intermediate material used for their manufacture are covered as to uses, properties, and chemical and physical tests. It is a worth-while reference book. E. M. Symmes

MARKET REPORT—DECEMBER, 1931

THESE PRICES UNLESS OTHERWISE SPECIFIED ARE THOSE PREVAILING IN THE NEW YORK MARKET, DECEMBER 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.	.14½
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.	.26½
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.	.06¼
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.	1.15
Bismuth, nitrate, 25-lb. jars......lb.	1.25
Oxychloride, boxes............lb.	2.95
Subnitrate, U. S. P., 25-lb. jars.lb.	1.35
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

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.	.55
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.	.32
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.	7.00
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.	.22$^{4}/_{5}$
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., bols.	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.	3.85
Lead acetate, bbls., white	lb.	.11
Arsenate, bbls.	lb.	.10
Oxide, litharge, bbls.	lb.	.10¾
Peroxide, drums	lb.	.20
Red, bbls.	lb.	.07¼
Sulfate, bbls.	lb.	.06¾
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.	.10½
Double, bbls.	lb.	.10½
Niter cake, bulk	ton	12.50
Nitrobenzene, drums	lb.	.08½
Oil, castor, No. 1	lb.	.10
China wood, bbls.	lb.	.07
Coconut, Ceylon, tanks	lb.	.03⅜
Cod, N. F., tanks	gal.	.26
Corn, crude, tanks, mills	lb.	.03⅝
Cottonseed, crude, tanks	lb.	.04
Lard, edible, bbls.	lb.	.11¼
Linseed, bbls.	lb.	.076
Menhaden, crude, tanks	gal.	.20
Neat's-foot, pure, bbls.	lb.	.09½
Oleo, No. 1, bbls.	lb.	.07⅝
Olive oil, denat., bbls.	gal.	.60
Foots, bbls.	lb.	.04½
Palm, Lagos, casks	lb.	.04¼
Peanut, crude, bbls.	lb.	.04½
Perilla, bbls.	lb.	.06¾
Rapeseed, bbls., English	gal.	.45
Red, bbls.	lb.	.07⅜
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.	.27
Palladium, metal	oz.	19.00
Para-aminophenol, kegs	lb.	.84
Para-dichlorobenzene	lo.	.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.	.42
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.	.08½
Binoxalate, bbls.	lb.	.14
Bromate, cs.	lb.	.35
Carbonate, 80–85%, calc., casks	lb.	.05
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.	.35
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.	.16½
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.	.05¾
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.	.05
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.	.22¼
Tin tetrachloride, anhydrous, drums, bbls.	lb.	.1605
Oxide, bbls.	lb.	.23
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.	3.65
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