



## EDITORIALS

### *Greetings from Our President*

I APPRECIATE the honor and responsibility that American chemists have given me. I wish to extend to every member of the AMERICAN CHEMICAL SOCIETY my best wishes for a prosperous and happy new year, and to all chemists outside of this organization the same good wishes, with the sincere request that they become a part of the AMERICAN CHEMICAL SOCIETY, thereby sharing the responsibilities of their profession and likewise receiving its benefits. The AMERICAN CHEMICAL SOCIETY has just completed its most successful year, and the plans for the future development of the SOCIETY will make membership therein of even greater value.

It is a source of pride to scientists that there is now more interest in industrial research than there has been at any other time in the history of our country. Let us hope that more and more attention will be accorded to science as a means of combating economic difficulties of national significance.

Let us likewise hope that industry will recognize the valuable relationship of capable teachers of science in our colleges and universities. These teachers are not only the source of industrially important raw material, pure scientific data, but also develop new talent and supply industry with its most essential raw material, well-trained research workers.

E. R. WEIDLEIN

### *On the Horizon*

IT IS fortunate that in the United States of America defeat in a fairly fought fight is not a disgrace. We shout loudly enough at our opponents in controversial matters, but we do not shoot at them. We are tremendously interested in political campaigns and each side uses to the full all its available resources, but after the tumult and the shouting die away we report on time for work the next morning and business goes on as usual.

According to the current writers, the United States is fortunate in yet another most important matter. Political events in other countries have lately strengthened the extremes almost to the destruction of the center. Here the last election has gone far toward destroying the lunatic fringe in politics. The extremes

have suffered. We are not likely to hear so much in the immediate future from the followers of Lemke, Townsend, and Father Coughlin, nor from the ultra-conservatives and the reactionaries. The disappearance from political consideration of these extremes has left us with a strong center, and that is something about which to raise the flag.

Some predict that from this strong center there are to emerge the parties which will contest for the next presidential election and that element which can control the existent well-nigh perfect political machine is the one likely to succeed. If this be true, may we not expect history to repeat itself and now that industry has turned from extremes of criticism to avowed intention to cooperate with the Government, the prospects are for the exercise of more conservative federal policies in the not distant future. There is much, then, concerning which to rejoice.

We regret that we do not have the space to reprint the "Basic Principles of American Industry" as enunciated following the annual convention of the National Association of Manufacturers held in New York in December. The basic principles, however, are set down somewhat as follows:

Better living, better housing, more of the necessities, comforts, and luxuries of life, steadier work, more certainty of a job, more security for old age. These are the natural desires of every human being. They are the progressive objects of American industry.

And then the pledge:

To continue to advance toward better living we as manufacturers pledge to the future our skill, our efforts, and our resources.

We pledge our cooperation to government—local, state, and national—in the furtherance of those measures which will promote the best interests of the American people.

Prosperity for a nation depends on productivity and peace. Productivity can be destroyed by internal dissensions, by labor conflicts, and by wars. Industry seeks an era of good feeling.

This does not mean that constructive criticism is a thing of the past. Every farsighted leader knows the value of a virile, honest, and critical minority. It does mean, however, that industry recognizes, perhaps as it never has before, the very great obligation which rests upon it, and the codes lately announced by it, based on principles calling for an era of good feeling both at home and abroad, are indeed encouraging.

But there are other responsibilities. No one can foretell just what course will be followed by the Administration, the responsibilities of which were tremendously increased as a result of the November election. The Congress must necessarily deal with recurring fiscal matters. Many of the emergency measures will automatically expire during 1937 and the future of this activity in the light of improved economic conditions will demand earnest and serious attention. Other legislation admittedly demands extensive amendment to make it workable and satisfactory, and there are certain to be many new bills introduced.

The professional man has a responsibility in helping to determine public policies, not only because of the technical contributions that have been made and the problems consequently involved, but because the type of counsel and judgment which he is trained to render is much needed. On several occasions we have urged chemists to take a proper part in political affairs of the day. If we note things not to our liking, surely we can do more toward correcting them in accordance with our viewpoint if we participate than if we remain aloof. Many a chemist who complains that he is unappreciated, that he is a member of a profession to which the community denies the proper recognition, makes no effort to become known for activity in civic matters and contents himself with beating a path from his home to his place of work and return. The chemist should first of all be known for his professional activities, but he can also be effective in civic enterprises without detriment to his chosen work, and indeed frequently to its benefit.

With economic conditions unquestionably better, whether measured by the shortage of skilled labor, the increased volume of business, improved employment conditions, or what not, and with industry disposed to do more than its share in the circumstance, the new year can be faced with greater ease and more enthusiasm for the future than has been the case in what seems a very long time. If we would all devote as much energy in the effort to help all of us go forward as we sometimes spend in developing a critical point of view, or even a grouch, we should be able to set our faces toward the sun and make real progress.

### *Planning Science*

WHEN daydreaming, have you ever answered such a question as: What would you do in research if surprised with a number of millions of dollars for the purpose? Undoubtedly, many would organize projects in science so fundamental as to require generations before the results would be applied. One great American scientist has said that all research to be justified must ultimately be useful and some others think that the word "ultimately" is providentially added to protect some of their friends whose research seems to be in corners so small as to possess little likelihood of utility. Still

others see in the immediate foreground and pressing for answer questions that at least to them are so important as to dwarf consideration of any others.

Now we all must admit that no one is wise enough to sort out from any list of research problems those which, when solved, will prove of the greatest value. Our scientific history is full of instances of research which seemed of no importance but which in a short time became the center of vital enterprises. It is admitted, too, that even in this day there is an attractiveness for many people in the mysticism which pervades certain branches of science. One of our chemists has remarked that progress in a science depends upon the extent to which its results profoundly affect the public, the number or proportion of the public influenced, and the rapidity with which these effects take place. The greater these factors, the slower the development. In his view this accounts for the almost static condition of the law and the great caution of medicine. Likewise it may explain the speed with which we have gone forward in mathematics, physics and quantum mechanics.

The American Institute of Physics, in a recent meeting celebrating the fifth anniversary of its founding, paid considerable attention to the place of physics in industry, and listened to an address by John Ely Burchard, vice president of the Bemis Industries, Inc., and a specialist in prefabricated dwellings, who had some things to say about the direction of such research. In closing his address he quoted Grosvenor Atterbury as follows:

What really interests us most vitally today? Is it the discovery that my umbrella, if projected through space at sufficient velocity, will actually become shorter, until, if Einstein's Theory is what it is cracked up to be it will disappear altogether? Scarcely. I can lose umbrellas fast enough as it is \* \* \* Now we are spending millions to build 200-inch telescopes to scan the universe and determine whether it is getting measurably smaller or incalculably greater. All of which, in the present state of the realm, seems hilariously useless, especially when you consider the millions who cannot afford decent homes because none of our great minds has ever been focused on the basic everyday problem of human shelter. Science needs an intelligent board of directors. With a small amount of such brains as are now focused on the speed with which the neutron penetrates the nucleus of the atom, and only 2 or 3 per cent of the money now devoted to research into the living conditions at the dawn of history, the cost of the poor man's housing today could be cut in half.

There are doubtless many who experience the same reaction when they look over any list of research undertakings and their appreciation diminishes in direct proportion to their knowledge of the specialty. We can all go back, however, to the admitted inability to prophesy when and when a bit of truth newly discovered may be the key to a pressing question.

Our hypothetical daydream question is occasionally put in real life, for we know of one or two groups which

have been asked almost overnight to outline how more money than they had ever dreamed would be available for their research could be spent with some justification. We wonder if the time has not come for stocktaking on a fairly broad basis, not with a view to criticising current research but to ascertain in the major fields of science the principal projects now in hand and what new work should be initiated from the point of view of answers needed now and with a long view towards the future. This is done in many laboratories, but their horizon must be more limited than would be that of a group who could gather in confidence reports of work in progress and out of the whole perhaps evolve a plan for nation-wide consideration. Such an outline would necessarily be largely confined to fundamental studies. Of these, some are certainly more promising than others, and the list could be segregated accordingly. One result would doubtless be that we know far less than we think we do and we might be surprised at the location of some points of weakness.

We think an example of the latter may be found in the field of psychology, and it is no fault of the psychologists. While realizing that what is most needed is to learn how to teach people to be adaptable, nevertheless there is a great need for further work that will enable those who train and those who employ labor to ascertain within reasonable limits the kind of work a man can be expected to perform with efficiency and some satisfaction to himself.

This country is now faced with a shortage of skilled labor. It is not unlikely that within a number of months it will even be looking for more unskilled labor, but, if we are correctly informed, throughout the depression little has been done in continuing research which will enable those interested to help labor by placing it where it can perform to the best advantage and earn the most rapid advancement. Some simple questions have been standardized that help, but there is ever so much more to be done.

There are some groups and organizations which ought to be in position to do such nation-wide planning for science, but we doubt if they will do it. We believe the AMERICAN CHEMICAL SOCIETY is peculiarly well fitted to undertake it for chemistry and we urge it as a SOCIETY project. Perhaps our sister societies can do the same sort of work for their specialties. Much can be done towards having plans ready when support becomes available and in the meantime guidance can be offered to many research workers.

### *Costly Literature*

ONE might think that, with the availability of technical literature, none of those interested in a particular subject need be deprived of prompt access to current publications. It would appear, however, that there are still people who prefer to pay an intermediary a high price for readily available papers rather than to

follow developments personally and choose for themselves.

There has recently come to our attention an enterprise which offers an information service, presumably on various specialties, offering to keep its clients informed on "new developments in manufacturing processes, new discoveries regarding new products, utilization of waste products, patents, formulas, etc., almost as soon as it takes place."

One report issued by this group in June, 1936, was composed of seven leading articles, all copied from "recent" literature, but five of them reprinted without credit from INDUSTRIAL AND ENGINEERING CHEMISTRY for 1934, and with abstracts taken from *Chemical Abstracts* of May, 1936. The illustrations were not reproduced and, even if they had been, at the price paid those receiving the report were given short measure. For a fraction of the cost of this report service (\$32 a year) the publications of the AMERICAN CHEMICAL SOCIETY may be obtained with promptness, and the recipient, by dint of a little reading, kept much more nearly up to date in his specialty.

In sharp contrast is the real service that is rendered by certain specialists in literature. Unlike the activity described above, which purports to be what it is not, there are certain groups which, for fees based on service rendered, prepare abstracts and references from a wide selection of literature with full data as to the place of publication of the original article. Then there are those who gather clippings from numerous publications on a unit cost basis, the undertaking being to supply such information from a far greater number of sources than a client might be expected to have available. Naturally, such clippings likewise indicate their place of origin and have as their principal merit wide coverage and promptness.

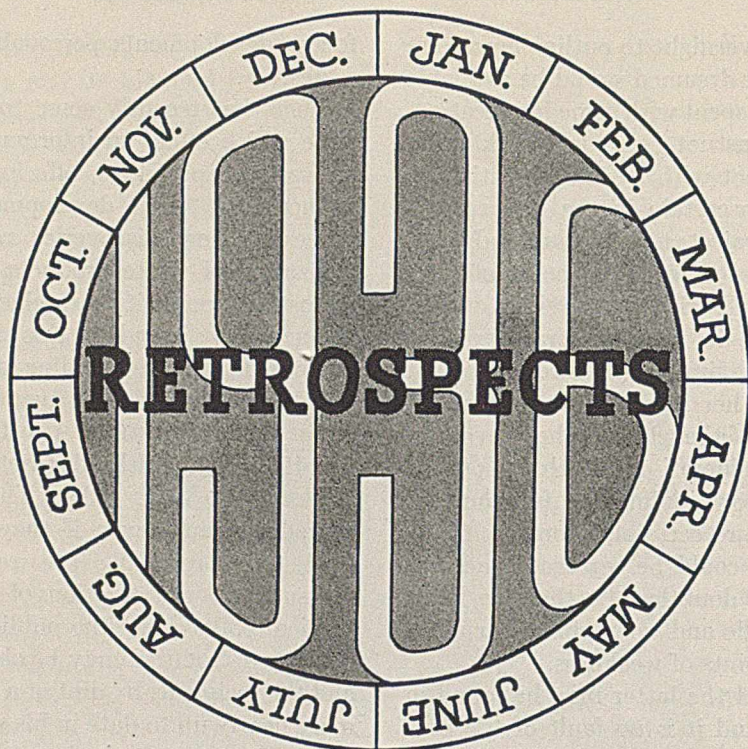
The value of literature is unquestioned, but sometimes cost may bear a strange relationship to it.

### *Committing Our Society*

THE question occasionally arises: Who can commit the AMERICAN CHEMICAL SOCIETY to a definite opinion or policy?

It would seem clear that, unless otherwise stated, the opinions of the Editor as expressed editorially are just that and nothing more. The SOCIETY can be committed only through the vote of its Board of Directors, the vote of the Council when in session, or the Council Committee on Policy when the Council is not in session.

To be sure, the President can speak in some matters with authority, and in others the Chairman of the Board of Directors, but on important questions either official is very likely to consult the Executive Committee of the Board of Directors or the Council Committee on Policy before making his statement, and in that case what is said carries the weight of the SOCIETY.



**T**HE year 1936 was an exception. The uncertainty attending a hotly contested national election on which marked differences of opinion were held failed to interfere in the least with the progressive improvement of business. This increased activity was particularly

evident in the equipment industry supplying capital goods, and in no part of it more so than in the chemical equipment field.

Long hesitancy to make capital expenditures through the depression years was overcome early in 1936 presumably by the threat of heavy taxation on undivided surpluses. Whether this threat was the actual ruling cause or whether the pressure of accumulated demand of itself forced the issue is difficult, if not impossible, to determine. However, the facts are clear enough. By the end of February a demand for chemical equipment and capital goods of all kinds far exceeding any that had been experienced for many years was making itself felt in every direction. The magnitude of this demand is practically impossible to determine accurately, but a few individual instances will suggest its effect. One company reported that from the first of the year to the middle of March there was more demand for its equipment than in the full years of 1934 or 1935. Another company found that before the first of July its profits on business completed were already sufficient to carry the increased overhead of its enlarged staff throughout the year. Similar reports were heard in all directions in the chemical equipment industry with not only largely increased domestic sales, but a growing demand for American chemical equipment abroad.

The situation of the chemical manufacturers and operators of chemically controlled processes was similarly encouraging. The change here was less marked than in the equipment field because at no time during the depression had demand for chemical products dropped to a low point comparable with that reached by the equipment industry. Indeed, it is difficult, if not impossible, to trace the course of the late depression with anything approaching accuracy from statistics of chemical production. The production curves of this industry were remarkably free from the pronounced rises and falls everywhere else in evidence.

### Employment

The changed situation with respect to employment in the chemical field became decided in 1936. Statistical analysis

of unemployment in this, as in other industries, is virtually impossible because of the almost complete lack of reliable figures. A survey made of the employment rolls of individual companies by the *New York Sun* revealed that in 1936 the companies classified as

"chemical" showed 109.5 per cent as many employees as the same companies in 1929. The probability is that this figure is low rather than high and that the number of employees in the chemical industry as a whole has increased somewhat more as compared with predepression years than this survey would indicate.

The employment situation for chemists of professional caliber reached a point early in the year where an actual dearth of men existed. The unreliability of most figures on this situation has been repeatedly stressed throughout the depression years. However, in 1936 for the first time since 1930 the schools of chemistry of the leading universities were visited by personnel scouts from the larger chemical companies. Selections were made early in the year from men to be available in June and, as early as November, scouts were already interviewing men to be available in the summer of 1937. At the same time there has been evident in the classified advertising of most chemical publications a decided increase in the number of employers seeking men. This increase was particularly marked during the last six months of the year and confirms the fact that well qualified men have again become actually scarce. The fact that the "situations wanted" columns are still long is considered by some to indicate that unemployment among chemists still exists to a rather pronounced degree. This interpretation is, however, not easily tenable since investigation shows that a majority of those responsible for "situations wanted" advertisements are presently employed and are seeking improvement.

### Patents

In the rapidly progressing chemical industry where many materials and new methods are being continually devised, the importance of trade-marks and patents looms large. Some of the decisions on these questions handed down by the courts during the year have emphasized points involving special interests of chemists and the chemical industry. It is not our purpose here to go farther in discussing these decisions than merely to point out these special interests.

The legal phases of such matters are beyond the scope of this discussion.

In the suit of United Chromium, Inc. *vs.* General Motors Corporation, the New Departure Manufacturing Company, and the Bassick Company, the question at issue was the Fink patent [U. S. Patent 1,581,188 (April 20, 1926)] for chromium plating. In the U. S. Circuit Court of Appeals for the Second Circuit, this patent was declared invalid, reversing the decision of the District Court. The point of interest in this particular decision lies in the fact that it is based on the question as to whether Fink or Udy was the first inventor of a successful chromium-plating process. In the early days of this art an interference in the Patent Office was declared between applications made by Fink and by Udy. Subsequently both applications came into the ownership of one company and the interference was dissolved by abandoning the Udy application in favor of Fink's already issued patent. It now appears in the decision of the Court that the two applications each disclosed a successful method of electroplating chromium and that evidence exists that Udy's first successful application of the process was made prior to Fink's. Such questions frequently arise in the work of chemists where a corporation or an individual seeks to make its position and control of a patented process stronger by purchasing the patents of others. It is often necessary on this account for the owner of two or more similar patent applications to decide which of them he will continue to issuance and which abandon. In this case the Court of Appeals decided that the choice between the Udy and the Fink applications was wrongly made, a situation which might readily arise in any organization which bases its operations on research. A rehearing on this case before the same court was granted on the basis that under the existing circumstances the rules of the Patent Office left no alternative to abandoning the Udy application in favor of the issued patent of Fink. Decision on the rehearing, handed down December 7, reaffirmed the same court's previous finding without opinion. Steps are being taken to appeal to the U. S. Supreme Court. What the final outcome in this particular case will be remains to be seen, but it emphasizes the necessity for the greatest possible caution before abandoning any of a group of patent applications for fear the wrong one may be brought to issuance and an untenable situation later created.

The question of the rights of the owner of a trade-mark in the coined name for a new synthetic material was again brought to the fore in the decision of the U. S. Circuit Court of Appeals for the Second Circuit in the case of Du Pont Cellophane Company *vs.* Wax Products Company. Although in a legal sense this decision did not "make law," it again emphasized the hazard of loss of trade-mark rights through the adoption of the coined name as a descriptive term. The issues revolved about the word "cellophane" in which the Du Pont company claimed trade-mark rights. In its decision the Court pointed out that despite the diligence of the Du Pont organization in its attempts to maintain valid trade-mark rights in the word "cellophane," the use of the word had become general as the descriptive name for sheeted regenerated cellulose. Consequently the decision states that the word "cellophane" can be used by anyone for any such sheeted cellulose so long as that use does not involve or imply fraud. In other words, if the user of the term cellophane uses it in such a way as to avoid implication that the product of another is that of the Du Pont company, such use is legitimate. This decision calls to mind other similar notable decisions, particularly relating to "aspirin" and "dry-ice," and emphasizes again the extraordinary care necessary to preserve trade-mark rights in the coined name of a new product, which can easily be lost through use as a descriptive word or name.

The question of a single court of patent appeals whose duty it would be to exercise jurisdiction on appeal over all matters having to do with patents was crystallized in a bill introduced into the Senate (S. 3823) during the second session of the Seventy-fourth Congress. This bill details the establishment of such a court to consist of a presiding judge and four associate judges, together with three permanent scientific advisers to the court. This matter of centering decisions on patents and patent law in a special court specially qualified for the purpose has often been raised and has met both with favor and opposition. Opposition ordinarily has come from the patent attorneys who feel that the establishment of such a single court would tend to immobilize patent law and prevent it from meeting the changing needs of the times. The proponents of unification of patent law in this way base their views primarily on a desire to avoid the conflicting opinions now frequently met in different courts of equal rank. Recently the American Institute of Chemical Engineers and the Association of Consulting Chemists and Chemical Engineers, among others, put themselves on record as favoring in principle the establishment of such a court of patent appeals.

In the meantime the question of thorough revision of the practice of the U. S. Patent Office has received renewed attention. Criticism of the present practice in granting patents is largely based upon the fact that the Patent Office serves a dual purpose. While the duties of the patent examiners are to determine the novelty and patentability of ideas presented, actually the Patent Office serves as the training school for those intending to practice patent law as attorneys. These two functions are by no means always compatible and men qualified for the service enter it at low pay with the expectation that after a reasonable period of training they can leave the Patent Office for more lucrative employment. This situation fosters a continually changing personnel, and men who have become fully qualified continually leave the service in the hands of others less skilled. President Roosevelt has indicated a strong desire to revise the practice of the Patent Office in such a way as to make it of greater service to the people and to industry in fostering material progress.

### Foreign Trade

The policy adopted by the Federal Government with respect to foreign trade has been the subject of bitter differences of opinion. The State Department has entered into trade agreements with foreign countries under which mutual tariff concessions and preferences in the matter of foreign trade have been exchanged. Opponents of this method of encouraging foreign trade have pointed out that our treaties with other nations contain what is known as a "most favored nation clause." Any concession in the matter of tariff given to one such nation automatically applies to all. The importance of this lies in the fact that such treaties are now in force between the United States and all of the principal countries of the world with the exceptions of Germany and Australia. The antiadministration forces have claimed, and have backed their claims with statistics, that the result of these trade agreements has been an immediate increase in our imports without a corresponding increase in exports. However, it is practically impossible yet to determine accurately the true facts in the matter since most of the trade agreements have been in effect for less than a year. Perhaps more complete statistics of imports and exports to the trade agreement countries will show a favorable balance of trade for the United States. In the meantime, the valid criticism of this method of handling questions of tariff is based on the constitutional provisions reserving matters of tariff to the Congress rather than to the executive branch of the Government

which, under the trade agreement plan, has in effect exercised the prerogatives of the Congress. So far, trade agreements of this kind with many nations, including France, Switzerland, Canada, Netherlands, and Finland, have lowered the tariff on numerous chemical products such as dyes, coal tar synthetics, rayon, cotton goods, wood pulp, and others. The net result, since these reductions are almost universally applicable, has been the equivalent of lowered duties to all principal producing nations.

### Industrial Developments

**PLATINUM HOARDING.** Restrictions on the hoarding of gold in effect now for some years have transferred the attention of speculators to platinum. To meet this demand for a valuable material for speculative hoarding, 3-ounce ingots of platinum certified as to weight and fineness have been struck off in large quantities and an active trade in these ingots has sprung up in 1936. The effect was to raise the price of the metal from \$35.00 an ounce in June to double that figure in September. The chemical industry is second to the jewelry business which uses 50 per cent of our platinum, and is followed by dentistry and electricity. The highest price of platinum in the American market was reached in 1923—\$116.54 per ounce. The lowest price in 1933 was \$30.99 per ounce. The present price (December 7) is \$46.00 per ounce.

**REPEATER MATCH.** In Sweden what is said to be the first really fundamental improvement of matches in many a year was announced in a new repeating match. It consists of a core containing the compounds ignited by friction as in the ordinary match head. This core is surrounded by a sheath of slow-burning chemicals. Struck in the usual manner the match burns slowly until the user blows it out. The match head composition is diluted with slow-burning chemicals so that its rate of combustion is no faster than the outer sheath. To relight, the core is merely scraped against a suitable surface just as with an ordinary match.

Although it is not expected to replace ordinary matches, the new development will probably become popular for pocket use and may even be carried in a special tube so that its purchaser will never find himself without the means to strike a light.

**GLASS.** Developments in the glass industry during the year have provided a new variety of glass of the Pyrex type sufficiently resistant to be used in frying pans and other similar utensils on top of the stove in direct contact with flame. The application of some of the modern glass wools of very fine fiber to the weaving of cloth has progressed considerably but is still more picturesque than practical.

**MANGANESE RECOVERY.** A new process for the recovery of manganese from ores containing as little as 10 to 15 per cent of that element has been developed by the Bureau of Mines. The process consists of electrolyzing a solution of manganese in sulfur dioxide. The economy of the new process developed by S. M. Shelton of the bureau is expected to make possible the recovery of manganese on a commercial scale from American ores.

**ALCOHOL.** A new method of dehydrating ethyl alcohol by use of salts, particularly sodium acetate, has been put into operation by the Commercial Solvents Corporation. This method avoids the use of strong alkalies and of toxic solvents.

The first plant in the United States designed to produce alcohol from grain for use primarily for motor fuel was put into operation at Atchison, Kans. The entire output of absolute ethyl alcohol has been consumed continuously in motor fuel in the Middle West. The total capacity of the plant is approximately 10,000 gallons of absolute alcohol per day, but production so far has averaged about half of this amount or less. The operation is fostered by the Chemical Foundation

as a large-scale experiment to determine the value of alcohol blends as motor fuel. Raw materials used have included numerous domestic sources of starch and sugar, among them such farm products as sweet potatoes, not heretofore used in commercial alcohol manufacture.

### Physical Chemistry

**MOTION PICTURES OF SPECTRA.** A new method of taking motion pictures through a spectroscope, developed during the year by David Richardson at Massachusetts Institute of Technology, greatly increases the sensitivity and accuracy of the spectroscope in detecting traces of elements. The record of the changing spectrum of a flame containing the material under investigation shows the presence of elements in such minute quantities as to cause merely a flash of color which might be overlooked by the observer and might be missed by a single photographic exposure. This increases extraordinarily the sensitivity of the already supersensitive spectroscope in analysis.

**POLARIZING PLATES.** Widely heralded during the year have been two developments of plates for polarizing light. One of these depends upon the formation of tiny crystals in an elastic medium. These crystals which are formed without definite arrangement are oriented by stretching the medium in which they have been formed, and this layer is then cemented between glass plates. By this method effective polarization is secured. The other method depends upon the formation on a surface, preferably glass, of a single large thin crystal. This thin crystal is protected by cementing upon it a separate layer of glass. The crystals used are understood to be iodine-substitution products of alkalooids. The application of these two ideas to the problem of suppressing glare is receiving active attention. At present such polarizing plates are used instead of more expensive Nicol prisms in scientific work, but the application in automobile headlights and windshields, in photography, and in many other places where the reduction in intensity of reflected light is desirable have been suggested.

**MODERN ALCHEMY.** In the realm of subatomic physics, new transmutations have been accomplished by bombarding the nuclei of atoms with neutrons, protons, and deuterons. These atomic bombardments take place in electric fields of extremely high magnitude ranging up to 16 to 17 million volts which provide enormous amounts of energy. Lauritsen of California Institute of Technology formed beryllium atoms from lithium atoms using proton bombardment. Lawrence and Cork of the University of California succeeded in transmuting tiny amounts of platinum into gold using deuterons as missiles. Pegram of Columbia University, using a slow-moving neutron, changed sodium atoms into magnesium. In this field of activity the most striking development has been in imparting radioactivity artificially to different atoms. So far more than forty elements have been used in these experiments and to each of them has been imparted an artificial radioactivity. In discussing this matter, Enrico Fermi of the University of Rome, a leader in the work, suggests that this method of studying atomic structure may have important values in producing radioactive materials of value in medical science in addition to its possibilities in creating new elements to be added to the present complete periodic system.

New light on the activity of enzymes has been provided by the work of Stern at Yale University who observed and photographed the transformations of catalase, a colored enzyme, in its attack on monoethyl hydrogen peroxide. This work shows for the first time the changes which occur progressively in the action of a catalyst, since during the course of the reaction catalase undergoes color changes.

## Medicinal and Pharmaceutical Chemistry

**TUBERCLE BACILLI.** R. J. Anderson who for some time has been engaged in searching for fundamental facts regarding tubercle bacilli has found that the germ produces disease in the human body by means of three chemicals, among the many it produces. These are a sugar, a protein, and an acid, all toxic to man and characteristic of the activities of this bacillus.

**VIRUS DISEASES.** Studies of the mosaic disease in tobacco plants indicate that the virus of a disease may be a protein. This conclusion, reached by W. M. Stanley of the Rockefeller Institute for Medical Research, suggests that the virus of a disease is not necessarily a living material. Repeated efforts to separate the protein from some impurity which might be the virus itself completely failed, although the methods used included repeated crystallization, high speed centrifuge, and extraordinarily fine grained filters. Without exception, the purified protein, whose molecular weight is considerably higher than that of other known proteins, produced the disease when applied to healthy tobacco plants. Apparently this leads to a new conception which may be important in combating other virus diseases.

**CARBON MONOXIDE POISONING.** Carbon monoxide was found to have a fatal effect in far smaller concentrations than had hitherto been considered dangerous. Harvey G. Beck of Baltimore reported to the American Medical Association during the year the observation of chronic carbon monoxide anoxemia, which he found in observations of seventy-nine patients "repeatedly subjected to sublethal doses of carbon monoxide at varying intervals over prolonged periods."

**PROTAMINE INSULIN.** Elliott P. Joslin, a leading authority on diabetes, speaking at the tercentenary session of the Harvard Medical School, described an improved treatment of diabetes resulting from the development of a new type of insulin which increases the effectiveness of ordinary insulin 8 times. "About a year and a half ago," he said, "the discovery of what is known as protamine was announced by Hagedorn of Copenhagen. This consisted in adjusting a mixture of insulin with protamine so that it had the same acid-alkali balance as that of the patient's body. With this new form the number of insulin injections could be reduced to only one in 24 hours. Further work had shown that the combination of zinc and calcium with the protamine more than doubled the effect, thus reducing the required injection in some cases by 87.5 per cent."

**VITAMIN B<sub>1</sub>.** Last year Robert R. Williams had progressed in his study of vitamin B<sub>1</sub> to the point where he could announce with confidence the structure of its molecule. In August, 1936, the goal which he had set for himself 26 years before when he began to devote his spare time to the study and investigation of the vitamin was achieved, and jointly with Joseph K. Klein the synthesis of vitamin B<sub>1</sub> was announced. Three years before, Williams, in association with collaborators, perfected the first successful large-scale method of extracting the substance from natural sources in pure crystalline form, but the synthesis of a material with an empirical formula  $C_{12}H_{18}N_4Cl_2SO$  presented enormous difficulties. At last this important "nerve vitamin," first suspected by Eijkman, crudely prepared in 1911 by Casimir Funk who named it "vitamin," and extracted in small amounts in pure form by Jansson working in Eijkman's old laboratory in Batavia, can be synthesized at a cost lower than that for its preparation from natural plant sources.

**SYNTHETIC SEX HORMONE.** Theelin, one of the two sex hormones responsible for female characteristics, was synthesized by Russell E. Marker and Thomas S. Oakwood at the Pennsylvania State College. This synthesis from ergosterol yielded a crystalline product. This is the third sex hormone

to be synthesized, the other two being corpus luteum, a female hormone, and testosterone, the male hormone. The importance of these materials in the control of sex irregularities promises much in the hands of the medical profession.

**PORPHIN.** The synthesis of porphin, the common chemical ancestor of hemoglobin, essential substance of blood, and of chlorophyll, the green coloring matter of plants, was accomplished by Paul Rothmund of the Charles F. Kettering Foundation at Antioch College. This synthesis is expected to lead to further syntheses of the porphyrins, the next intermediate toward both hemoglobin and chlorophyll.

**COBALT IN ANEMIA.** Minute traces of cobalt have been found essential in preventing certain types of anemia. Reports on this subject by Katsuji Kato of the University of Chicago, and Ross A. Gortner of the University of Minnesota before the National Academy of Sciences pointed out that this fact had been observed in physiological anemia in both children and cattle. The quantity of cobalt required is so minute as previously to have escaped detection.

**IDOCHOLEATE.** A new preparation of iodine, known as iodocholeate, which is nonpoisonous but possesses a high germicidal value, was introduced at the American Pharmaceutical Association convention during the year. The new compound is said to avoid the irritation caused by tincture of iodine and, because of its low volatility, to have a more prolonged effect.

**NEW CINCHONA DRUG.** Reports from the Philippine Government state that definite steps have been taken there to produce from cinchona bark a drug, called totaquine, for the treatment of malaria in an effort to break the Dutch monopoly of quinine. A report dated late in October states that 2 kg. of the drug are being produced daily from locally grown cinchona bark.

Synthetic resins are being used in the manufacture of a new type of contact lenses to replace eyeglasses. The actual lens is made of glass and fitted in a shield individually molded to the wearer's eyeball to be placed beneath the eyelids. Other glasses of this type have been made in which the lens is set into a blown glass shield, colored to represent exactly the white of the eye. The success in general use of these glasses, which are still expensive, remains to be seen. They are being used by actresses and others whose vision requires correction but who dislike spectacles.

Early in the year announcement was made of a new dental anesthetic (consisting of 2 parts sulfuric ether, 1 part ethyl alcohol, and 1.25 parts thymol by weight) which desensitizes the dentine of teeth to dental drilling. This anesthetic developed by Leroy L. Hartman, of the School of Dental and Oral Surgery of the College of Physicians and Surgeons, Columbia University, was given to the dental profession early in the year. Some criticism arose after the first announcement of this new material but it has been found effective in a great many cases.

## Miscellaneous

**NEW FINGERPRINTING METHOD.** A new effective method of developing fingerprints, important in criminology, utilizes iodine vapor for bringing out the latent image. Fingerprints on many surfaces which interfere with the powder method of development are brought out by blowing iodine vapor on the suspected spot. The apparatus is simple and consists of a glass tube containing iodine crystals through which the operator blows his breath. The iodine image is transferred to a bright silver plate by contact and is developed by exposing the silver plate to light from the sun or other actinic source. By this method it has been possible to develop and record fingerprints from polished furniture and other greasy surfaces as well as from finished paper.

New sources of petroleum believed to be far greater than those now known are being sought by L. R. Laudon, of the University of Tulsa, by charting the shore lines of geologically ancient seas. By carrying these observations beyond the present 2-mile depth limit of oil wells to about 30 thousand feet, believed to be the absolute bottom for oil, huge new potential oil resources are being revealed.

**PLANT HORMONES.** P. W. Zimmerman and A. E. Hitchcock have discovered that certain chemical substances are capable of arousing or stimulating activity in plants. Some sixteen chemicals and plant extracts induce growth in a few days when placed in the soil or when rubbed on growing plants. Carbon monoxide was the first pure chemical used experimentally to induce roots at unusual places upon plants. Since then other chemicals have been found effective, the best for the purpose being the synthetic naphthaleneacetic acid, four indole compounds, and phenylacetic acid. In addition, natural hormones extracted from roots, flowers, and ripening fruits proved effective. The first application of these discoveries is in starting roots on growing branches which may be cut off and planted as slips by nurserymen.

**COMPOSITION OF UPPER AIR.** As one of the results of the exploration of the stratosphere by the stratosphere balloon *Explorer II*, it was shown that the composition of the atmosphere at an altitude of about 70,000 feet shows virtually no change in the ratio of nitrogen to oxygen.

**BIBLIOFILM.** The Bibliofilm Service of the Library of the U. S. Department of Agriculture offers a new method of preserving and copying documents. This is particularly valuable as a method of duplicating documents of limited editions unavailable for general distribution. The method consists of photographing manuscript pages on standard motion picture film from which they can be read by the use of relatively inexpensive magnifying viewers. This is the first general application of the method of reproducing bulky manuscripts in highly condensed form. The cost is relatively small and the method makes many manuscripts generally available to an extent impossible before.

### Milestones

Technological advances become generally adopted so rapidly that one frequently loses sight of the speed of the process and novelty quickly wears off. A birthday party for Frederick Eugene Ives on his eightieth birthday (February 16, 1936) brought to attention the fact that the inventor of the halftone process of photoengraving is still living, so that within the lifetime of one man this most important fact in the present day spread of knowledge has grown from a mere idea to a universally valuable method of reproducing pictures.

Another anniversary of special interest celebrated during the year was the golden jubilee of Hall's process for the recovery of aluminum. During fifty years, easily within the memory of living men, aluminum has been taken by this process from the classification of rare and almost precious metals into the price class of the commonest, and from a rarity has become a modern essential.

1936 marked the centenary of the United States Patent Office, an event celebrated by leading scientists and inventors from all parts of the country and all fields of science and engineering. Included in the celebration were demonstrations of latest developments, some of which are still in process and foreshadow future developments.

Pope Pius formed a new Pontifical Academy of Sciences composed of seventy leading scientists in all fields. Selected for the honor of membership in the revived *Nuovi Lincei* are thirty-three Italians, six Americans, five each from France, Germany, and Belgium, four from Holland, three from Great Britain, two from Austria, and one each from Czechoslovakia,

Portugal, Argentina, Denmark, Norway, Poland, and China. Membership in this body is not limited to Roman Catholics alone. The American members are: Alexis Carrel, Rockefeller Institute for Medical Research; George David Birkhoff, mathematician, Harvard University; Robert A. Millikan, physicist, California Institute of Technology; Thomas Hunt Morgan, zoölogist, California Institute of Technology; George Sperti, physicist, Institutum Divi Thomae (Cincinnati); and Hugh S. Taylor, chemist, Princeton University.

During the year the following medals and prizes were awarded: Nobel Prize for Chemistry, P. J. W. Debye; Nichols Medal (by the New York Section of the AMERICAN CHEMICAL SOCIETY), W. M. Clark; Perkin Medal (by the American Section of the Society of Chemical Industry in New York), W. K. Lewis; Chandler Medal (by the Charles Frederick Chandler Foundation), W. F. Giauque; Willard Gibbs Medal (by the Chicago Section of the AMERICAN CHEMICAL SOCIETY), Roger Adams; Hillebrand Prize (by the Chemical Society of Washington), O. R. Wulf; American Institute of Chemists Medal, M. T. Bogert; Theodore William Richards Medal (by the Northeastern Section of the AMERICAN CHEMICAL SOCIETY), C. A. Kraus; AMERICAN CHEMICAL SOCIETY Award in Pure Chemistry, J. G. Kirkwood; Jacob F. Schoellkopf Medal (by the Western New York Section of the AMERICAN CHEMICAL SOCIETY), A. H. Hooker (posthumously); Chemical Industry Medal (by the American Section of the Society of Chemical Industry), W. S. Landis; Phillip A. Conné Medal (by the Chemists' Club, New York), D. D. Van Slyke; Pittsburgh Award (by the Pittsburgh Section of the AMERICAN CHEMICAL SOCIETY), A. W. Mellon and R. B. Mellon (posthumously); Herty Medal (by the Chemistry Club of the Georgia State College for Women), W. H. MacIntire.

### New Synthetics from Abroad

It would be improper to conclude this survey of the year without some reference to the fact that frequent announcements from abroad of new synthetic products have continually caused momentary stirs in men's minds. The announcement, for example, that a chocolate bar which looks like soap but tastes like chocolate has been synthesized in Germany from coal-tar raw materials and actually marketed, appears at first to indicate that our foreign brethren still lead us in cleverness. However, when this and similar announcements are checked and their significance is evaluated, the impression is largely nullified. Similar agitation has been caused from time to time by reports of new synthetic rubber-like materials abroad, which often turn out to be more interesting than important; in this field particularly the United States, with at least two such synthetic materials in large-scale production and use, definitely leads the world. It is, however, difficult, if not impossible under our economic system to combat the false impression which such offhand announcements from abroad create in the public mind. Laymen generally are not in a position as chemists most frequently are to answer such announcements by the query, "What of it?" More and more the real advances of industry based on scientific discovery in the United States are becoming everyday articles of commerce which the man in the street fails to recognize as synthetic. Yet the huge tonnages of synthetic products used in this country are daily increasing and their variety is widening at a rate far greater than can be equaled in any other country of the world.





# Research and Wall Street

SYDNEY B. SELF

Wall Street Journal, New York, N. Y.

CHEMISTS generally know very little about Wall Street and probably do not like it much. Wall Street, practically speaking, knows nothing about chemists but is very fond of them. Chemists are no doubt wise to stick to their test tubes for it has been said that a man cannot serve both God and Mammon, but Wall Street—that is, the financial community—has good reason to like the chemist.

Through research the chemist has created what is today one of the most stable and at the same time one of the most forward looking industries in the country, which produces mounting profits and generous extra dividends. Although there are a few wild animals running around Wall Street seeking whom they may devour, most of the financial community is composed of decent fellows whose job is to find safe and profitable places to invest the savings of their clients. Since these clients include investment trusts and insurance companies as well as individuals, their funds comprise a good part of the savings of the nation, and the problem of placing them where they will grow is difficult.

Men of finance probably do not fully realize the value of research, but they have a clear vision of its results as reflected in the satisfactory earnings of the chemical producers and the action of their stocks on the exchange. Chemists, on the other hand, in their concentration on the immediate job perhaps do not always appreciate the financial value of research but, since money makes the wheels go round, industrial research must in the final analysis justify itself in income accounts.

This, research has certainly done. However theoretical or intangible it may appear to the uninitiated, the record of the security markets shows clearly that the great industries leading in research work have also led in the recovery from the depression and stand first in stability.

A few years ago many serious people could be found who believed that America had finished growing. "We are growing old," they said. "There are no more frontiers and no new industries to pull us out of the slough of despond." They could not see, down in the depths of 1932, that research would open new frontiers not only in one but in a hundred industries. Competition is keener than ever before. Not only must costs be lowered and more efficient and better ways of doing things be found, but new products to widen markets must be developed. Since the black days of 1932 some companies and some industries have come back to peaks of prosperity even higher than in the old boom days and are looking forward to a still brighter future. Other companies and industries that have stuck to the old ways of doing things and have depended on natural recovery to bring their business back have not recovered even to what used to be considered



TRADING FLOOR OF THE NEW YORK STOCK EXCHANGE

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normal. Research is the primary cause of the difference between the two groups. There has been no single major product that has pulled us out of the last depression as the automobile did after the 1921 depression. Research workers in all fields, but most notably in chemistry, have developed new methods, new technique, and new products that have made obsolete a large part of the old routine. Industry has not yet caught up with the advances made in the laboratory during the depression, and the public is still farther behind. Further expansion of the chemical industry should come as some of the more recent products of laboratories attain greater general use.

The leading chemical companies this year have reported earnings well ahead of the boom time profits of 1929. This record showing in earnings has been achieved in spite of the fact that the average of chemical prices is still close to the lowest levels in history. It has been made possible directly as a result of research which has improved technique so as to cut costs, found new uses to increase volume, and developed new products when the older ones began to approach at least temporary limits in profits.

LET us look at the record of the chemical industry in the stock market. Has research paid? Leading chemical stocks over the past few years have done relatively much better than the general run of stocks.

Table I shows the action of leading chemical stocks on the New York Stock Exchange since 1932 in comparison to the Dow-Jones averages which reflect the action of the market as a whole as revealed by a group of leading stocks.

According to the table, in the first three years of market recovery, chemical stocks advanced from 1.3 to 4.2 times as much as the general market average. From March, 1935, to November, 1936, the advance was not as striking although most of the stocks in the chemical group held their own in spite of the large advances they made earlier in the bull market. Four out of nine of the stocks in the table did better

earnings available for dividends of most of the leading chemical companies are also close to or above record levels.

Table II shows the record of dividend payments of a group of leading companies in the chemical group since 1929.

Stocks marked with an asterisk have been split up since 1929, and past dividend payments have been adjusted to the present number of shares. Air Reduction was split three for one this year; Dow Chemical was split five for one in October, 1929, and one and one-half for one in July, 1934; Monsanto Chemical was split two for one in July, 1929, and two for one in April, 1934.

TABLE I

Company	Price		% Rise from 1932	Ratio of Rise to Dow-Jones Av.	Price, Nov., 1936	% Rise from 1935	Ratio of Rise to Dow-Jones Av.
	July, 1932	March, 1935					
Air Reduction	31 $\frac{1}{2}$	108 $\frac{1}{2}$	243	1.8	346 <sup>a</sup>	220	2.4
Allied Chemical	45 $\frac{1}{2}$	129	172	1.3	241	87	1.0
Atlas Powder	7 $\frac{1}{2}$	36 $\frac{1}{2}$	386	2.9	77	111	1.2
Commercial Solvents	4 $\frac{3}{4}$	18	278	2.1	16 $\frac{3}{4}$	-7	...
du Pont	22 $\frac{3}{4}$	88	293	2.2	180	105	1.1
Hercules Powder	14 $\frac{3}{4}$	72	390	2.9	132	83	0.9
Mathieson Alkali	10 $\frac{1}{4}$	23 $\frac{3}{4}$	132	1.0	38 $\frac{1}{2}$	62	0.7
Monsanto Chemical	16 $\frac{1}{2}$	114 $\frac{1}{2}$	599	4.2	194 $\frac{3}{4}$ <sup>a</sup>	70	0.8
Union Carbide	16 $\frac{3}{4}$	44 $\frac{1}{2}$	173	1.3	104 $\frac{1}{2}$	134	1.5

<sup>a</sup> Showing effect of stock dividends.

than the average market in the past year. (American Cyanamid and Dow were not included because figures were not available.)

Atlas Powder, du Pont, Hercules Powder, and Monsanto Chemical all did better than twice as well as the market averages in the recovery. Union Carbide and Air Reduction kept well ahead of the general advance. Allied Chemical and Mathieson Alkali, which have not laid as much emphasis on research as some other companies and deal mainly in heavy chemicals, just held their own with the general market. Commercial Solvents, which did about twice as well as the average in the first period, has fallen behind the market during the past year because of particular circumstances affecting this company.

Aside from stock market appreciation, the long term investor has fared well in chemical securities, receiving a fair income through the depression and record dividends in this year of recovery. Incidentally, although the new tax on undistributed income has affected dividend policies this year,

OF THE eleven companies listed, all but one, American Cyanamid, which was caught in the middle of a major expansion program, paid common dividends through the depression. Five of these companies, Air Reduction, Dow Chemical, du Pont, Hercules Powder, and Monsanto Chemical, paid larger dividends in 1936 than in 1929. Union Carbide's recent declaration of 80 cents quarterly also places it ahead of the 1929 dividend rate. Air Reduction, Dow, and Monsanto paid out more in 1935 than in 1929. Allied Chemical has maintained the same rate for many years. Mathieson, in the heavy chemical group, has not recovered to 1929 levels.

On the whole, the best dividend records have obviously been made by the companies leading in research. Air Reduction, while undoubtedly fortunate in its industrial position, has kept in the forefront by its research staff.

Allied Chemical has had an excellent financial record for the past fifteen years although it has not been a leader in research, but, in comparison to du Pont which was about the same size as Allied Chemical in 1921, its record is less brilliant. Allied Chemical this year paid around \$14,000,000 in common dividends; du Pont paid well over \$60,000,000. It is true that at least half of du Pont's income is currently coming from its General Motors investment, but its chemical income is also running far ahead of 1929 and far ahead of Allied Chemical's. General Motors, too, is an outstanding example of the utilization of research to its fullest extent by a great corporation.

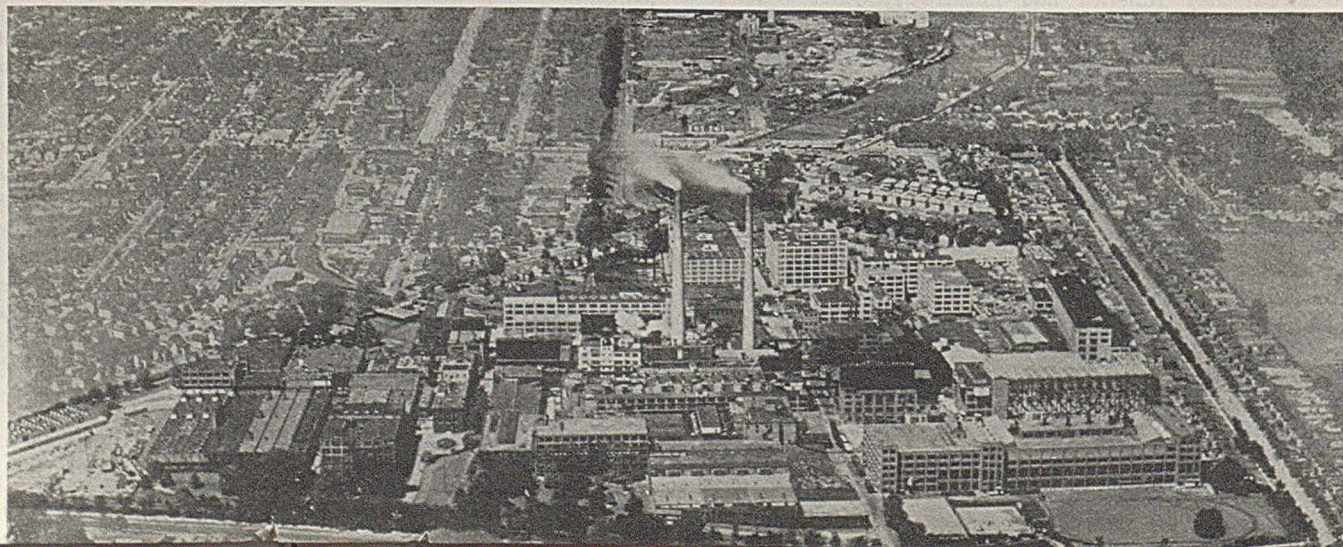
Dow, Hercules, and Monsanto are among the leaders in research, which has benefited stockholders materially through the widening and diversification of their business. Hercules is perhaps the outstanding example; if this company had depended only upon its original powder business it would not be making record earnings today.

RECEIVED November 30, 1936.

TABLE II

	1936	1935	1934	1933	1932	1931	1930	1929
Air Reduction*	\$2.50	\$1.83	\$1.50	\$1.25	\$1.00	\$1.50	\$1.50	\$1.41
Allied Chemical	6.00	6.00	6.00	6.00	6.00	6.00	6.00	6.00
American Cyanamid	1.00	0.55	0.25	None	None	None	1.20	0.80
Atlas Powder	3.50	2.00	2.00	None	0.75	4.00	4.00	5.00
Commercial Solvents	0.80	0.85	0.60	0.60	0.60	1.00	1.00	0.80
Dow Chemical*	2.20	2.00	1.66	1.33	1.33	1.33	1.33	1.20
du Pont	6.30	3.45	3.10	2.75	2.75	4.00	4.20	5.92
Hercules Powder	5.25	3.50	3.50	2.25	2.00	3.00	3.00	4.00
Mathieson Alkali	1.50	1.87 $\frac{1}{2}$	1.50	1.50	1.62 $\frac{1}{2}$	2.00	2.00	4.00
Monsanto Chemical*	3.25	1.50	1.05	1.00	0.61 $\frac{3}{4}$	0.61 $\frac{3}{4}$	0.61 $\frac{3}{4}$	0.62
Union Carbide	2.30	1.55	1.20	1.05	1.75	2.60	2.60	2.30

AERIAL VIEW OF THE PLANT OF EASTMAN KODAK COMPANY, ROCHESTER, N. Y.



# The Modern Cigaret Industry

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A discussion of the magnitude and importance of the domestic cigaret industry is given. Supporting statistics are presented, including some which show the leading part played by the industry in furnishing governmental revenue. The cultural methods and the chemical composition of those types of domestic tobaccos utilized in cigaret manufacture are reviewed. Mention is made of the commercially important types of cigarets. Domestic leaf cigaret tobaccos are extensively used in cigaret production, but the uniqueness of national taste confines the industry largely to the blended cigaret. Manufacturing methods, packaging, hygroscopic agents, flavoring materials, and cigaret paper are discussed. The composition of cigaret smoke and current aspects of its physiological effects are considered. The mutual need of the industry and the scientist for each other is pointed out.

**T**HE cigaret came into vogue in the United States after the Civil War, largely through the appeal to the smoking tastes of returned campaigners who had been introduced to flue-cured "makings" at Durham and other North Carolina markets. For the most part, the initial popularity of cigarets was not associated with the ready-made variety. Cigarets made in this country in the early days of the industry were composed largely or entirely of flue-cured tobacco. Next there came aden and for cigarets containing high proportions of so-called Oriental (more properly,

Levantine) tobacco. This picture was again changed about 1912 when the blended cigaret, as we know it today, started to gain a firm foothold. The exploitation of this type has really effected the enormous growth of the domestic cigaret industry, with the result that it now constitutes the bulk of sales, other types of cigarets dividing a relatively small market. Depending on the formulas of different manufacturers, the blended cigaret is composed of varying proportions of flue-cured (U. S. types 11 to 14), Burley (U. S. type 31), Maryland (U. S. type 32), and a number of Levantine types, such as Macedonian, Latakia, and Samsoun. A typical blend is somewhat as follows: flue-cured, 60 per cent; Burley, 15; Maryland, 10; and Levantine types, 15. Some of the more inexpensive blended brands omit the Levantine types, with a proportionate increase in one or more of the domestic types. The other types of cigarets are as follows:

1. Virginia cigarets are made wholly of flue-cured tobacco.
2. Egyptian cigarets are manufactured in Egypt from Levantine tobacco; they have become popular elsewhere. The terms "Egyptian" and "Turkish" are often used to designate similar cigarets made in this country and elsewhere.
3. Russian cigarets contain Levantine types of tobacco; they are made with a hollow mouthpiece, provided with a plug of absorbent cotton.
4. Mentholated cigarets contain substantially the same mixture of tobacco as blended cigarets, but menthol dissolved in a suitable solvent is sprayed on the tobacco prior to manufacture.
5. Denicotinized cigarets contain a blend of tobaccos from which a part of the nicotine has been removed by various processes. Thus far the removal of nicotine has been imperfect, and in the treated products we find about half as much nicotine as in the ordinary brands of blended cigarets. The average nicotine content of popular blended nondenicotinized cigarets is about 2.5 per cent; the authors' analyses show that the so-called denicotinized cigarets contain 1.03, 0.89 per cent nicotine in brand A; 1.29, 1.29 per cent in brand B; 1.44, 1.40 per cent in brand C; 1.27 per cent in brand D; and 0.65 per cent in brand E. Brand E, with the lowest nicotine content, is an Argentine product; the others are all domestic. The nicotine values given are in good agreement with those reported by another laboratory (11, 12).
6. The Cuban and Porto Rican types contain tobaccos very similar to those commonly used for cigar manufacture. The authors recently examined five brands of Mexican cigarets. Three of these contained cigar scrap; two were blends of Virginia and Burley tobaccos.
7. Perfumed cigarets have a very limited market.
8. Hand-rolled cigarets are sufficiently popular to make them an item of some importance. For this purpose flue-cured tobacco of the cheaper grades is generally used. Some smokers prefer to "roll their own" from pipe tobacco.

It is not easy to account for the great popularity of the blended cigaret over other types, particularly when we recall that Bogen (?), in pointing out the fallacies of the "blind-fold test," showed that persons are not able to distinguish between different brands of the same type, and that in some cases they even make mistakes in differentiating between types. Advertising has had a considerable part in keeping the blended cigaret constantly before the attention of the consuming public, but this factor does not seem entirely responsible. Nor can the natural tendency of a nation to use domestic agricultural products be held responsible, for on this basis we might expect the Virginia cigaret to be the leader, whereas the blended cigaret contains a substantial proportion of Levantine tobacco. Persons who are themselves smokers and have had long practical experience in various phases of the tobacco industry feel that flue-cured tobacco produces smoke which gives the impression of hotness. Smoke from Levantine tobacco, highly odorous and aromatic as it is, is not pleasing to all smokers. Probably by a judicious blend of the proper tobaccos, the more striking individual smoking characteristics of each have been repressed and the resultant aroma and taste have been found palatable

by most cigaret smokers in the United States. The blended cigaret is, however, not the national cigaret of all countries. The leading brands in England and Canada, for example, are composed of flue-cured tobacco; the Chinese also favor cigarets of this type. Cuba and many of our South American neighbors smoke cigarets prepared largely from cigar types of tobacco. Some of the European countries favor Turkish cigarets; in certain other nations cigaret types not described in this article are in demand.

### Magnitude of the Industry

In recent years the volume of production of standard-size cigarets in the United States has been very large. The years 1935 and 1936 witnessed the greatest production in the history of the industry. Since 1910 production has increased over fifteen-fold (52), as follows:

Year	Cigarets Produced	Year	Cigarets Produced
1910	8,644,335,407	1931	117,064,214,494
1915	17,964,348,272	1932	106,632,433,834
1920	47,430,105,055	1933	114,874,217,470
1925	82,247,100,347	1934	129,976,333,581
1929	122,392,380,846	1935	134,607,741,257
1930	123,802,186,217		

A further idea of the size of the domestic cigaret industry may be obtained from the census of manufactures for 1935 (55), as given in Table I.

The production of tobacco is widely distributed throughout the world, and good tobacco, of highly reputed types, comes from all quarters of the globe. In rank of importance the tobacco-producing areas of the world (30) are Asia, North America, Europe, U. S. S. R., South America, Africa, and Australia. The political divisions rank in the following order in thousands of quintals (1 quintal = 100 kg.):

United States	6453	Greece	549
British India	6300	Italy	444
U. S. S. R.	1692	Philippines	418
Brazil	1100	Canada	390
Japan	665	Turkey	354
Netherland Indies	556		

The past 20-30 year period, in which cigaret manufacture has increased enormously, has brought greater and greater tobacco production. During that time the United States acreage devoted to flue-cured tobacco has increased from 341,000 to over 1,000,000 acres (39). The demand during this period has been increasing generally, so that the value of tobacco exports has been constantly above the pre-war value. The indices of exports based on the 1914 value for export crops are given in Figure 1.

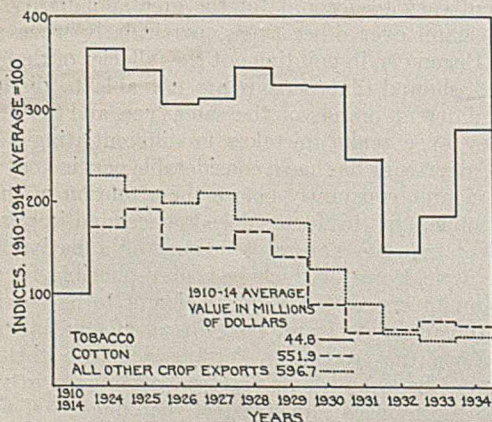


FIGURE 1. INDICES OF U. S. EXPORTS BASED ON 1910-1914 AVERAGE VALUES

In 1935 the only curtailment schedule in operation affecting tobacco was that enforced in the United States in connection with the AAA program (30). Differing from similar

limitation programs operating in wheat and rubber, in that it did not have the coöperation of other producers, it left the way open to increased production in other countries. The adaptation of popular types in new regions is constantly going on, and the shift of focus from one type to another, accompanying changes in tobacco-consuming tastes, has happened in the past and is not again impossible. Consequently an assured domestic supply of a variety of types is in the manufacturer's interest. Tobacco from the United States goes into cigarets quite generally all over the world, whereas the export of manufactured cigarets is curtailed by the individuality of national tastes and monopolies.

In point of value, tobacco is the second ranking United States crop export and ranks fifth of all exports. The value of manufactured cigaret exports in 1934 was \$6,144,000 (47).

### Domestic Cigaret Tobaccos

The U. S. Department of Agriculture in its official classification system recognizes twenty-six different types of American-grown tobacco (19); in addition, many other types are grown in various parts of the world. Each type has its peculiar uses, but this discussion will be confined to those types that are being utilized by the domestic cigaret industry. No type of tobacco is employed exclusively for any one manufacturing purpose, although it is true that each type has its principal use, while certain grades of the type are diverted to other lines of manufacture. Thus flue-cured tobacco is used chiefly in cigarets, but appreciable amounts also go into chewing tobacco and pipe mixtures. Certain grades of Burley tobacco are essential for making blended cigarets, but still greater quantities are used in pipe tobacco and a considerable amount in chewing tobacco. Maryland is largely a cigaret type, but to some extent is used for other purposes; this is also true of the Levantine types, some of which are employed for blending in the more expensive pipe mixtures.

TABLE I. CENSUS OF U. S. CIGARET MANUFACTURES (55)

Year	No. of Establishments	No. of Wage Earners	Wages	Cost of Material, Fuel, Electricity, Revenue	Value of Products	Value Added by Manufacture	Federal Tax
				Thousands of dollars			
1933	27	22,544	13,835	503,560	637,776	134,216	356,209
1935	26	24,346	18,238	637,643	802,201	164,558	385,459

To a greater degree than most other flora, the tobacco plant is responsive to such factors as soil, fertilizers, climatic conditions, variety of seed, and curing methods. A set of conditions, which by long experience has been found to be ideal for producing the characteristics demanded by the trade in one type of tobacco, may not be the conditions required to produce another type. The result is that the geography of production of different types is rather definitely defined. This does not mean that any given type can be grown in only one magic area; but, if the type is to be successfully translocated, the conditions in the new area must approximate the conditions in the original area. An example is the successful growing during the last decade or two of good quality flue-cured tobacco in southern Ontario (48), as well as other parts of the world, such as China, Australia, Rhodesia, and Nyasaland. An instance of unsuccessful translocation is seen in the several attempts made to raise Levantine types of tobacco in this country, notably in California and the Carolinas. One of the authors had occasion to smoke cigarets made from tobacco grown in South Carolina from a seed variety brought from Greece; although they were agreeable smokes, they were



PULLING-UP ROOM WHERE TOBACCO IS REMOVED FROM HOGSHEADS (IN FOREGROUND) AND PLACED IN ORDERING MACHINES (ALONG WALL), WHERE ADDITIONAL MOISTURE IS ACQUIRED

actually novel and quite unlike cigarets made from imported Levantine tobacco. Also, in any given tobacco-growing area the difference in weather during different growing seasons produces crops which are not identical in smoking characteristics. This fact is well recognized by tobacco buyers, with the result that one year's crop may be more in demand than another. For example, hot, dry weather favors a high nicotine content; in the leaf web of a sample of 1930 Maryland tobacco the authors found 2.12, 2.26 per cent nicotine, whereas in a sample of the same grade and type from the 1932 crop they found 0.86, 0.83 per cent nicotine.

Table II gives statistics covering the production for a number of years past of the three domestic cigaret types of tobacco. In recent years the four types of flue-cured tobacco have accounted for a high proportion of the total domestic production of all types combined (Table III). This is due to the fact that so much is used in blended cigarets and also to the popularity of flue-cured as an export type. Corresponding data for Levantine types are not available, but imports in recent years have amounted to about 35,000,000 to 40,000,000 pounds annually. During 1934, the last year for which statistics are available, 54 per cent of the total production of flue-cured (54), 30 per cent of the Maryland, and 8 per cent of the Burley were exported. Thus the export trade is an important activity. The apparent inconsistency suggested by the decline in production of cigaret types contrasted with the increase in production of cigarets is accounted for in Figure 1, which shows a recent declining trend in exports of leaf tobacco.

Figure 2 presents those areas in which the domestic cigaret types are grown.

Flue-cured tobacco is subdivided into U. S. type 11, grown in the Piedmont section of Virginia and North Carolina, and U. S. types 12, 13, and 14, grown in the coastal plain areas of the Carolinas, Georgia, and Florida. These four types have their individual smoking characteristics (13), owing to differences in growing conditions. Types 12, 13, and 14 are thin tobaccos of light yellow color; type 11 is a thicker, darker, and more aromatic tobacco. Throughout the region fairly uniform methods of growing and curing are practiced. Plants grown in beds are transplanted to the fields during the spring.

Sandy and sandy loam soil types prevail throughout the area, and the fields are prepared with moderate applications of commercial fertilizers (20). Much labor is involved during the growing season, including hand "suckering," similar to the practice on tomato plants in some seasons. The method of curing the leaves when they have attained the desired state of ripeness explains the origin of the term "flue-cured." The leaves are pricked (plucked from the stalk as they ripen) and strung on sticks about 4.5 feet long, although in a few sections the whole plant is cured. The sticks are placed in the flue-curing barn, constructed of logs, frame, or tile. A fire box is provided which is fired with wood from outside the barn, and the smoke is passed through an iron flue extending along the ground from the fire box to the other side of the barn and

TABLE II. PRODUCTION OF THREE DOMESTIC CIGARET TYPES OF TOBACCO (53, 54)

Year	Flue-cured, Type 11	Flue-cured, Type 12	Flue-cured, Type 13	Flue-cured, Type 14	Burley, Type 31	Maryland, Type 32
	1000 pounds					
1919	180,273	183,808	101,182	11,621	300,348	19,575
1920	297,328	219,998	86,955	11,687	287,716	27,125
1921	168,244	127,904	56,190	6,456	175,677	18,590
1922	231,058	126,345	54,010	4,026	276,399	20,020
1923	268,787	205,359	97,359	9,231	340,356	21,384
1924	205,264	139,080	61,480	31,511	295,778	24,480
1925	212,984	215,369	95,612	51,119	277,840	24,690
1926	226,621	212,176	79,717	41,558	288,793	26,040
1927	284,216	261,950	110,623	62,000	176,227	26,176
1928	245,608	284,700	121,462	87,329	269,136	20,460
1929	262,928	265,319	128,438	93,067	342,213	24,750
1930	294,094	314,882	145,292	109,008	347,297	16,625
1931	230,701	254,697	109,238	63,079	464,955	31,540
1932	141,040	152,218	69,624	13,275	313,604	26,272
1933	237,237	291,600	148,092	61,654	383,342	20,400
1934	198,350	230,850	100,192	35,128	282,999	23,418

TABLE III. PRODUCTION OF FLUE-CURED TOBACCO (53, 54)

Year	Total Production	Flue-Cured Production	
	1000 lb.	1000 lb.	% of total
1930	1,647,377	864,276	52.5
1931	1,583,567	657,715	41.5
1932	1,026,091	376,157	36.6
1933	1,377,639	735,583	53.6
1934	1,095,662	563,520	51.5

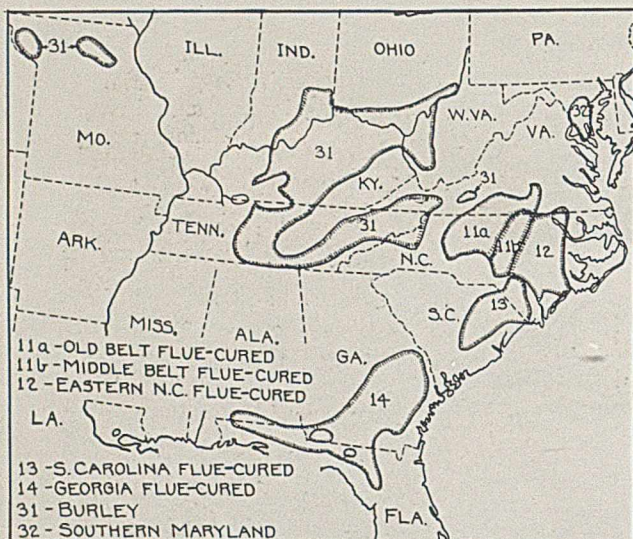


FIGURE 2. CIGARET-TOBACCO-GROWING DISTRICTS OF THE UNITED STATES

back again. Maintenance of the proper temperature is an art acquired by experience. The curing period is about 5 days. After the leaves have become sufficiently yellow, the heat is increased until first the leaves, then the midribs, are dry. The leaves, after absorbing enough moisture to permit handling, are graded, made into "hands" consisting of about twenty leaves tied at the butts with another leaf, and are then taken to an auction warehouse in one of the numerous tobacco market towns where buyers representing the tobacco companies compete at auction sales. Chemically, flue-cured tobacco is low in nitrogenous constituents and high in carbohydrates, particularly reducing sugars. Numerous analyses have been reported by Garner, Bacon, and Bowling (20) and Darkis, Dixon, and Gross (13); the analytical values obtained in the Mellon Institute are in good agreement with the findings of these investigators.

Of the numerous strains of Burley tobacco, the one most in favor for some time past has been the so-called White Burley, indicating the light color of the plants. The cultural operations in raising Burley are much the same as those followed in the flue-cured district; unlike flue-cured, Burley does not thrive on the lighter soils but requires rich soils such as are found in the blue-grass region of Kentucky. When the plants have yellowed up to about the middle, they are ready to be harvested; they are then cut off near the ground and attached to sticks, which are spaced at proper intervals in the curing barns. Curing, which is accomplished under the influence of the surrounding air, requires 6 to 8 weeks, depending on the prevailing weather and the skill of the farmer in regulating ventilation; the cured leaves vary from light brown to reddish brown in color. Very damp weather is apt to necessitate warming and drying the air, although not nearly to as great an extent as in the flue-curing process; this heating is accomplished by means of coke stoves (salamanders). After curing, the leaves are stripped from the stalks, graded, made into hands, and marketed like flue-cured tobacco at auction warehouses. Burley is a high-nitrogen and low-carbohydrate tobacco. Since fewer analytical data seem to be recorded for this type than for others, some of the authors' analyses of cigaret grades of Burley tobacco samples (kindly furnished by E. J. Kinney, of the Kentucky Agricultural Experiment Station) are given in Table IV; they supplement the findings of Shedd (43).

Maryland tobacco is grown on sandy soils not unlike those on which flue-cured tobacco is produced. Growing operations resemble those used for the other types; like Burley, it

is air-cured. After stripping and making into hands, the tobacco is packed into hogsheads and sold in this condition at Baltimore, which is the only market for this type. Maryland tobacco is a light brownish red. Like flue-cured, it is a low-nitrogen and high-carbohydrate tobacco, but it is distinguished from flue-cured by its low nicotine and reducing sugar and its high cellulose contents (20). It burns excellently and produces a relatively neutral flavor and aroma; it therefore blends well with other types and confers good burning qualities on cigarets.

A detailed account of the growing and handling of these three types of tobacco is given by Garner et al. (20), Shedd (44), Kinney (28), and Posey (36).

Burley and flue-cured tobaccos, after purchase by tobacco companies at auction, are redried (by means of heat), then brought to 10–12 per cent moisture, packed into hogsheads, and allowed to age in warehouses under prevailing weather conditions for two to three years, when the aroma has developed to the point where the tobacco is ready for manufacture. Maryland tobacco is aged similarly but without the previous redrying. The only study of the aging of cigaret tobacco has been given in the recent extensive paper of Gross et al. (15), who demonstrate that, in the aging of flue-cured tobacco, certain of the carbohydrate and nitrogenous constituents show significant but not gross changes. They hypothesize that both darkening of color and development of aroma during aging may be due in part to the slow formation of melanoidins.

TABLE IV. ANALYSIS OF BURLEY TOBACCO (LEAF WEB ONLY)

	1932 Crop, %	1933 Crop, %
Nicotine (4)	3.05 – 3.44	3.53 – 3.79
Total nitrogen (37)	2.78 – 3.11	3.24 – 4.08
Nitrate nitrogen (56)	0.001 – 0.033 <sup>a</sup>	0.23 – 0.46
Ammonia nitrogen (57, 59)	0.19 – 0.23	0.11 – 0.28
Amide nitrogen (57, 59)	0.18 – 0.27	0.40 – 0.46
Protein (21)	7.00 – 7.62	6.13 – 7.62
Ash	19.88 – 19.99	18.24 – 19.71
Pentosan (4)	7.36 – 7.76	8.51 – 9.43
Reducing sugar (4)	0 – 0.38	0
Carbohydrates hydrolyzed by acid (4)	6.92 – 6.98	5.78 – 6.52
Ether extract (4)	7.20 – 8.27	5.70 – 6.15
pH (58)	5.45 – 5.47	5.50 – 5.62

<sup>a</sup> This is a particularly low nitrate nitrogen content.

### Criteria of Cigaret Excellence

The following outline presents concisely the criteria of excellence of a blended cigaret. The neglect of any one of these factors will be apparent in the loss of quality:

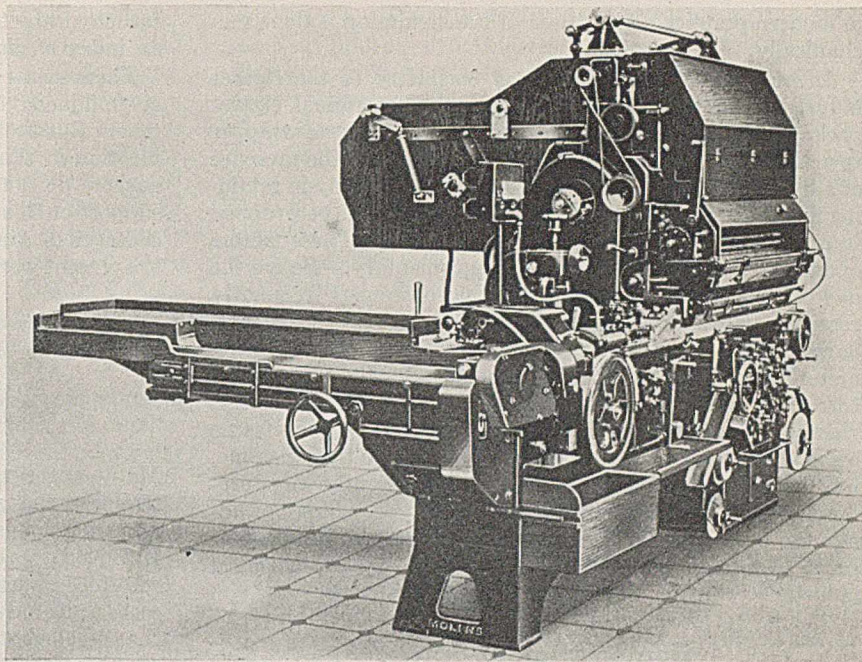
- I. Quality of tobacco
  - A. Selection of tobacco which, on aging, is capable of acquiring a fine aroma
  - B. Live color, characteristic of the type
  - C. Proper composition of ash conducive to cohesiveness, completeness of burn, and absence of charring
    1. Absence of deleterious constituents, chlorides in particular
    2. Presence of calcium, magnesium, and potassium in optimum ratio
- II. Blend—selection of grades and incorporation of aromatic types to attain a pleasing smoke
  - A. Qualities sought
    1. Dry and sweet
    2. Mellow
    3. Mild and sweet
  - B. Qualities to be avoided
    1. Acrid and puckery
    2. Green and burnt
- III. Flavoring to confer pleasing odor suggestive of tobacco
- IV. Paper and adhesives
  - A. A good grade of cellulose which does not yellow and whose combustion products are neutral

- B. Filler content as low as compatible with opacity
  - C. Adhesive to conform to the requirements of the paper
- V. Competent manufacturing procedure
- A. Modern machinery, properly operated
    - 1. Tobacco shreds
      - a. Long shreds give compact appearance and good drawing qualities to the cigaret
      - b. Small shreds result in poor ends and loss of burning quality
    - 2. Adjustment of operations to secure proper packing
    - 3. Rigid control of moisture fundamental to working properties of tobacco, and to smoking and keeping qualities following manufacture
  - B. Packaging
    - 1. Physical protection of the product
    - 2. Attractive design
    - 3. Preservation of quality

### Manufacture

In the handling of cigaret tobacco, the control of moisture is of prime importance. Before the tobacco is packed for aging, it is reduced to a 10–12 per cent moisture content, as previously indicated. After the long aging period, when the tobacco is ready for manufacture, the moisture content is insufficient to permit handling without undue shattering. The tobacco is therefore moistened to about 20–25 per cent for stemming (the stems are not usable in cigaret manufacture and are utilized by companies that manufacture nicotine); for cutting, it is necessary that the moisture be reduced to about 16–19 per cent. It is later dried to a moisture content of close to 12 per cent before the cut tobacco goes to the cigaret-making machines. Not much deviation from this optimum figure is permissible because at a lower moisture content the cigarets tend to reach the consumer too dry for smoking; if the moisture is much over 12 per cent, molding may occur. The nicety with which the moisture content can be controlled is one of the major advances of the cigaret industry in recent years. By a rapid and accurate electrical conductivity method, it is possible to determine the moisture content at various stages of manufacture. A detailed account of modern cigaret manufacturing practice is given in the recent article of Cone, Hatcher, and Greenwald (10).

The raw materials of cigaret manufacture are leaf tobacco, a hygroscopic agent, a small amount of flavoring materials, and cigaret paper. Because it is low in sugar and because it carries the flavoring materials better, the Burley part of the cigaret blend is selected to receive the manufacturing liquids. These liquids are of two kinds, casing or hygroscopic agents (which will be discussed later) and flavoring materials. A variety of flavoring formulas is used, comprising sugar, honey, essential oils, spices, and various extracts. The addition of flavor is often made by dipping the Burley into a heavy sirup of commercial glucose or brown sugar and honey that also contains the less volatile flavoring ingredients. The excess solution is pressed out between rolls; the tobacco is dried, cooled, and moistened. The volatile constituents of the flavoring liquid are applied in spray form, to either a part or all of the blend. Cocoa, chocolate, licorice, ginger, cinnamon, tonka, vanilla, coumarin, molasses, rum, brandy, maple sirup, certain esters, angelica, oil of anise, oil of juniper, oil of cloves, honey, and sugar are among the flavoring agents which have been used. The practice of flavoring, which contributes



CIGARET MACHINE WHICH PRODUCES AS MANY AS 1600 CIGARETS PER MINUTE

more to the pleasing odor of a newly opened cigaret package than to the aroma of the smoke, is encountered in producing other forms of tobacco and is old in the tobacco-products manufacturing art. The idea held by some that inorganic nitrates are added is erroneous, for good burning qualities are easily controlled by a proper selection of tobaccos, including the excellent-burning Maryland tobacco already mentioned. Formerly much controversy raged over the presence of "dope" in cigarets, either in the tobacco or the paper or both. This, like many other fallacies, has now largely collapsed. Thurston (51) some years ago investigated the possible presence of narcotics in cigarets and found none.

Cigaret paper is a good grade of cellulose derived from linen, hemp, or ramie, admixed with enough filler, usually calcium carbonate, to give opacity and to control the rate of combustion of the paper (27, 42). The authors have examined samples of five cigaret papers by the methods of the Technical Association of the Pulp and Paper Industry (49). No starch, rosin, or glue sizing was found, and the fibers were linen with, at most, only traces of wood pulp or ground wood. In four samples the filler was calcium carbonate; in the fifth it was a mixture of calcium carbonate and titanium dioxide. In the latter sample, the filler was present in much smaller amounts than in the other samples, owing to the greater efficiency of titanium dioxide in producing opacity.

An achievement in which the cigaret industry may well take pride is its high degree of mechanization, thereby bringing about savings that have taken the cigaret out of the luxury class and have made it the companion of rich and poor alike. The cigaret industry in its early days was operated almost entirely by hand labor. Its first step in the direction of modern mechanization was taken soon after the Civil War, with the invention of the Bonsack cigaret machine (1). From that time to the present the cigaret machine has been in a constant state of evolution, until today machines are in daily use that are capable of turning out 1200 to 1600 cigarets per minute. Other operations in the cigaret factory are carried on largely by machinery. Only the handling and stemming of the leaf tobacco require much hand labor, and

in modern practice a great deal of the stemming is done mechanically.

An outstanding contribution of chemistry to the cigaret industry is in the field of packaging. The original cigaret packages were made of paper or cardboard, with no wrapper to assist in the retention of moisture. Although the presence of a hygroscopic agent in the tobacco assists greatly in retaining moisture, it is also important that the package be wrapped in a material highly impervious to moisture. These factors operating together are mutually supplementary. Before the day of wrappers, it was inevitable that customers frequently received packages of cigarets so dry that they gave hot, harsh, unpleasant smoke. Much of the aromatic flavoring material was lost along with the moisture. The first step in correcting this defect was taken when, through chemistry, glassine paper became available. Further progress came when Cellophane, more impervious to moisture than glassine, was marketed at a reasonable cost. More recently, moisture-proof Cellophane has replaced the older type. Superior adhesives, especially the Cellosolves, to be used with moisture-proof Cellophane have also been furnished by the chemical industry.

### Composition of Smoke

Some of the substances which various investigators have reported as being present in cigaret smoke are as follows: aldehydes including furfural (7), carbon monoxide (16, 26), hydrogen sulfide (3, 65), hydrogen cyanide (3, 61), methyl alcohol (34), diacetyl (40), hydrocarbons (62), resins (29, 64), ammonia (6), arsenic (23), and, of course, nicotine. The researches on the amount of nicotine in smoke are so numerous and the results so divergent, ranging from almost none to nearly all the nicotine contained in the tobacco (rather obvious errors can be detected in some of the procedures), that only the recent careful work of Jensen and Haley (25) will be mentioned. They point out the fundamental technic for obtaining smoke samples reproducible with respect to nicotine content. These investigators have clearly demonstrated that the nicotine content of smoke varies inversely with the moisture content of the cigarets, that with strong puffing more nicotine comes over in the smoke, and that there is considerable condensation of nicotine in a cigaret stub. Smoke which the smoker draws into his mouth has an acid reaction; that which goes into the air from the end of the cigaret is alkaline. Acidity of cigaret smoke is a subject which has recently been brought to public attention. The authors have examined a number of the well-known brands of blended cigarets by smoking them under carefully controlled conditions in a machine which imitated natural smoking and by absorbing the products of combustion in water. The pH of smoke solutions prepared from the several brands studied was always of the same order of magnitude. By steam distillation from strongly alkaline and strongly acid portions, respectively, followed by titration, total volatile bases and total volatile acids were determined. Ratios of volatile acids to volatile bases were computed. The results show that differences between individual experiments on the same brand are as great as the differences between brands. The acidity of smoke from good cigaret tobacco has been reported by several workers (5, 18, 45, 46, 63). Shirokaya (45) regards the acidity of the smoke as proportional to the quality of the tobacco and proposes adding small amounts of hydrochloric acid to poor cigaret tobacco. Shmuk and Kolesnik (46) also believe that the reaction of the smoke is a true indicator of the quality of the tobacco, alkalinity indicating a poor quality. They say that a high protein content is accompanied by high alkalinity of the smoke, whereas a high carbohydrate content leads to low alkalinity. They therefore propose the ratio of

carbohydrate to protein (the so-called Shmuk number) as an index of cigaret tobacco quality.

There seems to be a widespread impression that "strength" or "mildness" of cigarets is dependent on the nicotine content. But Rolleston (38) indicated that the importance of nicotine in this connection has been overemphasized. The authors do not believe that a definite correlation exists; in support of this view, the following approximate nicotine percentages of a number of types of cigarets, taken both from the present work and that of others (7, 11, 24, 50), are given:

Type of Cigaret	Approx. % Nicotine
Blended	1.9-2.7
Virginia	2.5-3.4
Levantine	1.0-1.5
Denicotinized	0.8-1.4
Porto Rican	0.8-1.2

Many experienced smokers regard Virginia cigarets as a strong smoke, and they are indeed high in nicotine. On the other hand, many smokers also think Levantine and Porto Rican cigarets are strong, but both types are notably low in nicotine. Nicotine or its decomposition products or both, seem to be only two of many factors involved in determining the so-called strength of a smoke; when the chemistry and physiological action of tobacco smoke are better understood, they may prove not to be the main factors. Recently, the question of irritation by cigaret smoke has received increasing consideration by smokers. Certainly the nonirritating smoke can be as pleasant as any other, and in the end result it seems probable that low irritation and mildness can be considered substantially synonymous.

### Physiological Effects of Smoke

As already stated, cigaret tobacco in process of manufacture is treated with a hygroscopic agent in order that the product may better retain its moisture and so not reach the consumer in dry ("stale") condition. Glycerol has been the time-honored material for this purpose. On theoretical grounds some other compounds ought to serve equally well or better, and since 1933 diethylene glycol has found use as a hygroscopic agent. The replacement of glycerol by this compound seems to be one of the most notable chemical advances that has been made in cigaret technology. The donor of the authors' fellowship has been the pioneer in this scientific development and use of diethylene glycol in cigaret manufacture.

Recent research (32, 33, 60) has shown that smoke from cigarets containing diethylene glycol is much less irritating than smoke from cigarets containing glycerol. Properly prepared smoke solutions were instilled into the test membrane, the conjunctival sac of rabbits; the degree of irritation was measured by the extent and duration of the resulting edema. The hygienic utility and value of diethylene glycol as applied to cigaret manufacture are indicated by the work of Flinn (17). This investigator conducted a series of tests in cooperation with a group of physicians, most of them nose and throat specialists, on human subjects selected because they had one form or another of congestion considered to be associated with smoking. The findings were that the troubles were eliminated or considerably benefited when the patients were changed from their customary glycerol-treated cigarets to those containing diethylene glycol. Most of the patients, on being changed without their knowledge to the same blend of tobacco containing glycerol instead of diethylene glycol, soon returned to the original congested condition.

Some extensive biochemical studies that have been made on cigaret smoking have followed blood sugar changes and respiratory quotient. The early impression was that ciga-



ret smoking raised the blood sugar value. This has since been refuted by Dill, Edwards, and Forbes (14), who reported that smoking one cigaret is without effect on blood sugar, lactic acid, and respiratory quotient; there is, however, a small increase in basal metabolism. The popular belief is that the appetite is decreased by smoking shortly before a meal. Failing to find any basis for this belief in the blood sugar change, Dill and co-workers call attention to the work of Carlson and Lewis (8) who found inhibitions of the gastric hunger contraction (dependent upon stimulation of nerve endings in the mouth) following smoking. The inhibitions may vary in intensity and duration, and are only slight for a mild cigar or a cigaret but may be prolonged following a strong cigar or a pipe.

An extensive review of the medical literature on smoking practice was published by Schrupf-Pierron (41). A number of pathologic conditions are described in which the symptoms were alleviated when the use of tobacco was discontinued. At the same time it is pointed out that, in addition to an aggravation resulting from the use of tobacco, a possible underlying source of aggravation should not be overlooked.

Citations are available (2, 31) of investigations on the bactericidal action of tobacco smoke. Appleton and Lehner (2) found that the smoke from a cigaret bubbled through diluted saliva reduced the bacterial count by 35 per cent.

Notable because of the distinguished character of the group considered, it is of interest to cite the testimony collected by O'Shea (35). Men of outstanding ability and distinction in various professional, scientific, and technical pursuits and administrative capacities were asked to state their opinion on smoking with regard to personal aspects, their observations on others, and their attitude toward smoking by men under their direction. Smokers and nonsmokers were about evenly divided among those replying, and the answers indicated that, although a few felt that they smoked in excess, the consensus of opinion was that the pleasure derived outweighed any possible harm. Many had seen men of outstanding ability in smoking and nonsmoking groups and were reticent to draw any distinction with regard to ability on the basis of

smoking; in all but two instances smoking habits were said to exert no influence in considering candidates for positions. In the same study were included several other groups, and it was shown that among high school students the relative standing of smoking and nonsmoking students is not predictable from the comparative scores in intelligence tests. The intelligence tests show a slightly higher score for the smokers, reproducible with four different types of tests and in five different cities, whereas scholastic standings show a partial correlation between smoking habits and standing, indicating that smoking is a factor but not the exclusive reason for lower standing of smoking students.

To some extent preconceived individual ideas are responsible for the enjoyment to be derived from smoking. It is in this respect that the influence of custom and social usage exhibits itself. In numerous instances the attraction of charm and social grace that may accompany cigaret smoking has been mentioned. Certainly there are not many social customs adapted to the restricted compass of conversation that allow of so much grace and expression of gesture. To many persons the attraction of smoking, with the accompanying active manipulation, is the real motive for smoking.

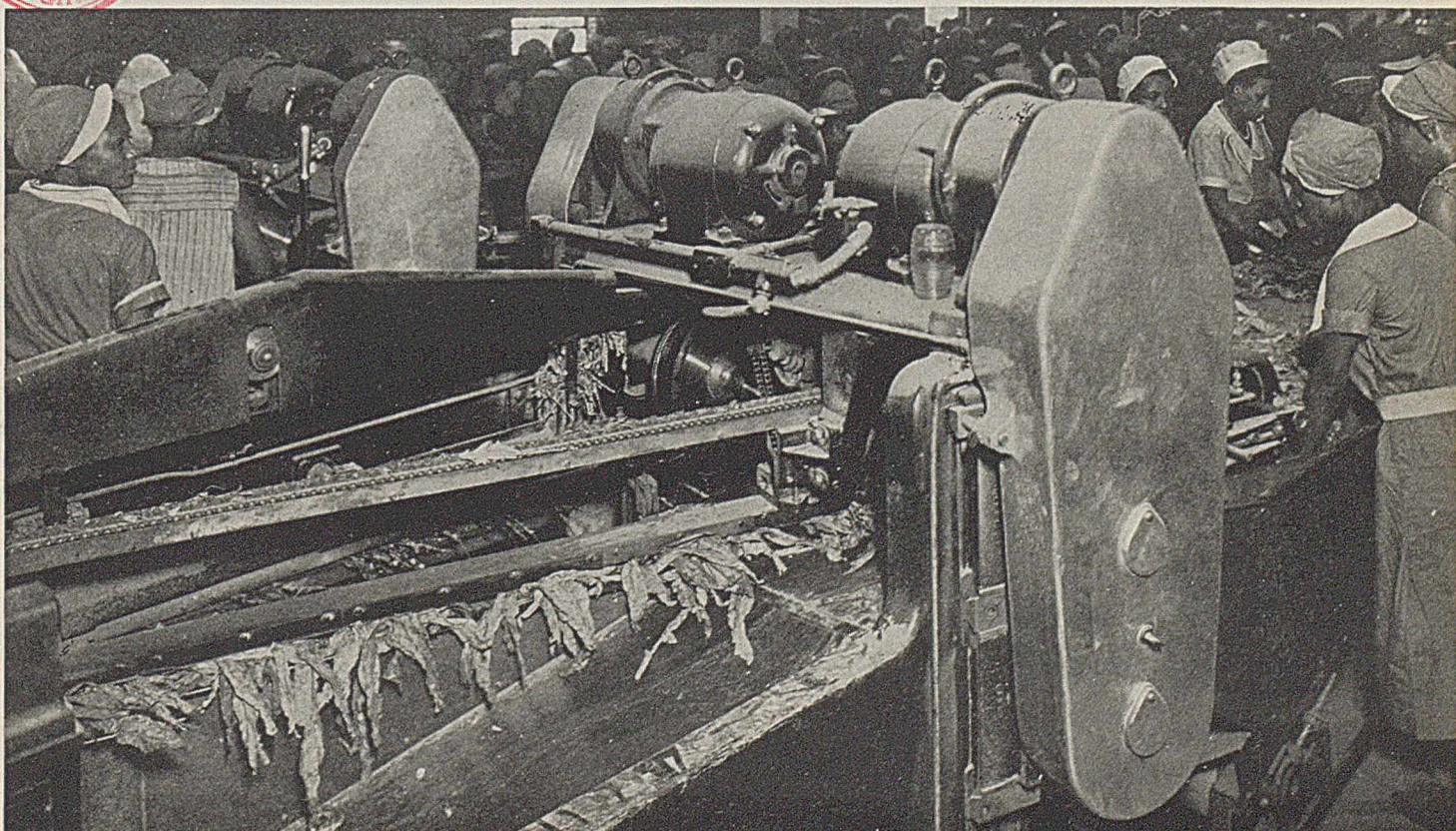
To this end the prime qualification sought in a smoke is that it be pleasant. If the noxious constituents are kept down, tobacco will continue to win its own way. In good tobacco there are many likable qualities; under some circumstances some are masked that still remain to be brought out in the smoke. The rise of the blended cigaret may be cited as an instance in point. It has been pointed out previously that blending has made a more desirable smoke by producing a cigaret whose reaction is more pleasing.

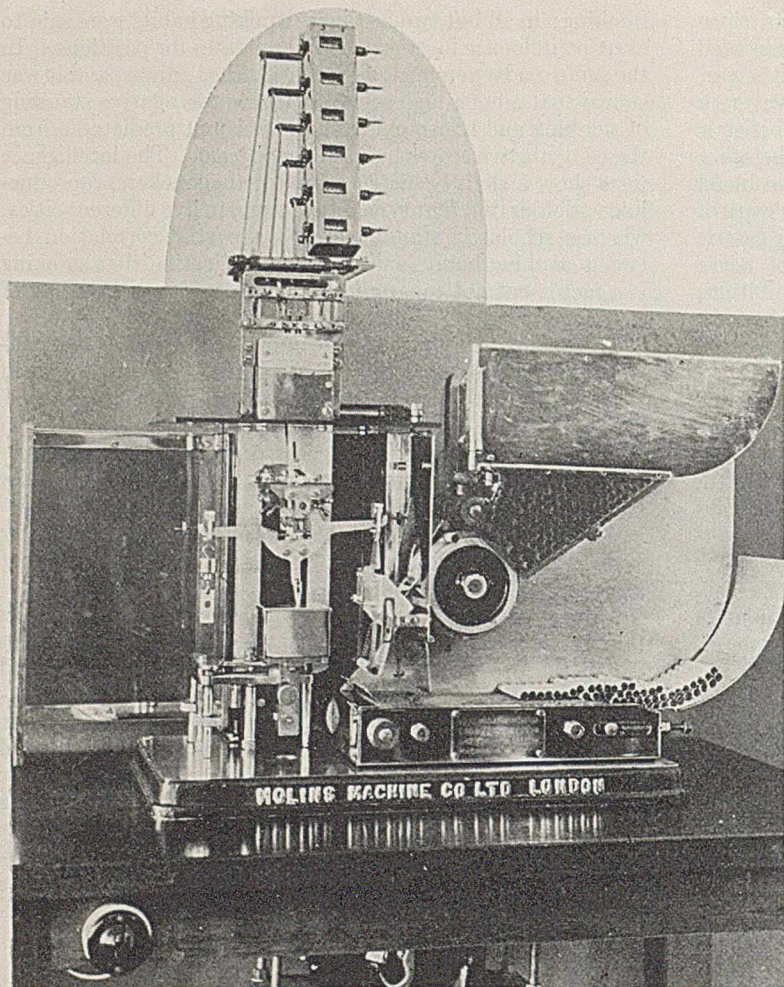
From a social point of view, there is need for a better understanding of the chemical nature of cigaret smoke and of its effect on human beings; this is a subject on which the knowledge is as yet quite incomplete.

### Revenue from Cigarets

Table I shows that the value added by manufacture is roughly 100 per cent of costs and that federal taxes are ap-

STEMMING MACHINES GREATLY INCREASE THE QUANTITY OF TOBACCO HANDLED, BUT THE DIVERSIFIED NATURE OF THE OPERATIONS REQUIRES SUPPLEMENTARY HAND LABOR





AUTOMATIC SCALES FOR COUNTING OUT AND WEIGHING CIGARETS AND RECORDING THE RESULTS

proximately two and one-half times the value added by manufacture. The importance of this source of income in federal economy is well illustrated by comparing the income received from all tobacco revenues with the highest source of federal revenues (22), income taxes (figures are for June 30, 1935):

Income tax, individual	\$527,112,506
Income tax, corporation	572,117,896
Cigaret manufacture	385,459,570
Gasoline	161,532,292
Total income and miscellaneous internal revenue	2,773,213,213

Generally, the world over, tobacco revenues rank first or second in importance as a source of governmental income of this class. Of the European countries the greatest portion so received was 22.5 per cent in Yugoslavia in 1934, while the average was around 15 per cent. Two systems of regulation are generally in force in regard to tobacco sales.

The relative advantages of state control and private operations may well be compared by considering the percentage of national revenue obtained through the sale of tobacco under the two systems. Those countries in which tobacco is sold under monopoly include Austria, France, Czechoslovakia, Hungary, Italy, Japan, and Spain. The tobacco monopoly yields the greatest fraction of the national income in Italy, where the return to the state for the year 1934 was approximately 15 per cent.

From the point of view of the consumer, a unique situation exists in present-day cigaret selling. Of the nominal sum that the consumer pays for a package of cigarets, 40 to 60 per cent represents federal and state taxes, from the residue

comes the largest lump sum payment for the maintenance of the news and light fiction media and the second largest sum toward broadcast entertainment. The liaison services, publicity, advertising, and radio broadcasting, are most extensively used by the cigaret manufacturers. From these agencies there are derived widely diffused public entertainment and service in the form of light fiction, news, and radio programs.

### Role of Science

Science has been and will continue to be of great service to the cigaret industry. As early as 1922, Chesley (9) described how chemistry was being successfully applied in the solution of the problems of one large manufacturer. Many but not all the problems can be so answered. The present well-stabilized supply of raw material has been attained through the efforts of chemists, agronomists, plant pathologists, and physiologists, and other scientists on the staffs of state and federal experiment stations who have made noteworthy contributions to tobacco culture, with the result that the companies are enabled to obtain leaf tobacco with the color, texture, aroma, burn, etc., which are desirable. Then there is the mechanical engineer, through whose efforts the industry has obtained constantly better machinery.

In the future, mechanization will undoubtedly proceed even further than it has to date. We may reasonably expect an increasing use of chemical and physical control of materials used in cigaret manufacture, as well as an increasing use of science in solving the numerous problems which arise from time to time in any large business. The chemical nature of the complex tobacco plant itself and the changes which it undergoes when cured and aged are still fruitful fields of research for the biochemist.

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RECEIVED August 27, 1936. The authors are Industrial Fellows of the Philip Morris & Company, Ltd., Inc., Industrial Fellowship at Mellon Institute.

# Vapor-Phase Hydration of Ethylene

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A PREVIOUS paper from this laboratory by Sanders and Dodge (7) gave the first definite proof that ethanol could be synthesized in significant quantities by the purely catalytic, vapor-phase hydration of ethylene. An approximate value for the equilibrium constant for the reaction at one temperature was established, and new data on catalysts were presented. Calculation of the equilibrium constant by thermodynamic methods yielded widely discrepant results, depending on the particular thermal data chosen. It appeared desirable, therefore, to continue the investigation of the equilibrium in this reaction in order to obtain a more accurate value of the constant at some one temperature and also to secure values over a range of temperatures.

This paper presents values for the equilibrium constant,  $K_p$ , for the vapor-phase hydration at 7 to 11 atmospheres and 320°, 350°, and 378° C., along with some new observations on catalysts which were obtained incidental to the main problem.

After the work to be reported was well started, two papers (2, 9) appeared which overlap somewhat the work done in this laboratory. However, inasmuch as results in this field have been scanty and very conflicting, checking results by independent investigators are desirable.

## Thermodynamic Calculation of Equilibrium Constant

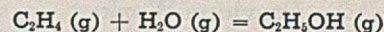
Sanders and Dodge (7) reviewed the situation on the thermodynamic calculation of the equilibrium constant and

Equilibrium in the hydration reaction has been investigated at 7 to 11 atmospheres pressure and at 320°, 350°, and 378° C. The results agree well with those of Stanley, Youell, and Dymock, and both sets of data are well represented by the equations:

$$\log_{10} K_p = 2100/T - 6.170$$

$$\Delta F^\circ = 28.20T - 9600$$

which refer to the reaction:



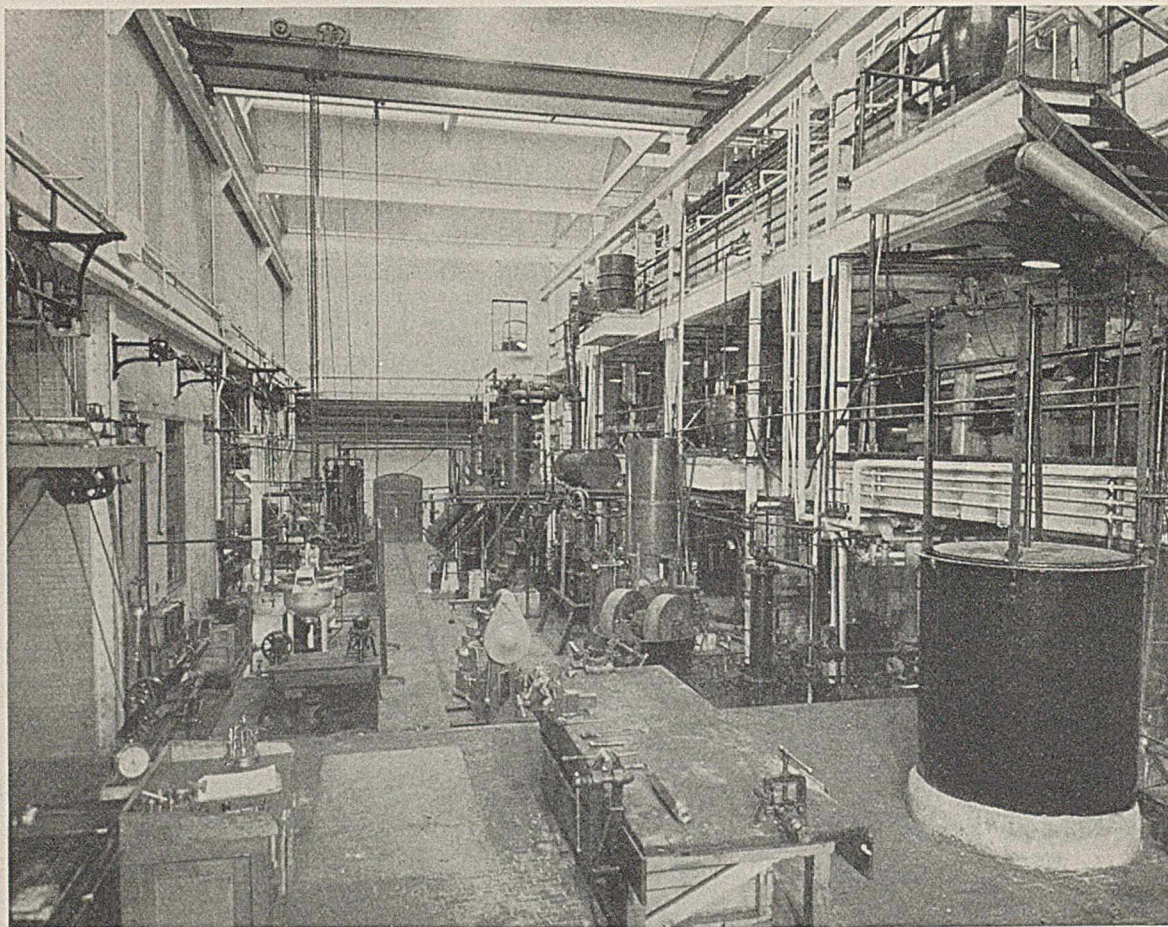
Some new observations on the behavior of various catalysts for the dehydration of ethanol are also presented.

came to the conclusion that this method was of little value because of the widely divergent results obtained. The present authors have made further calculations using other combinations of thermal data, some of which became available after the earlier paper was published. The results confirm the conclusions already reached.

Calculated values for  $\Delta F^\circ$  (standard free energy change) for the vapor-phase hydration reaction at 298° K. varied from -3025 calories per mole to +1168, corresponding to a  $K_p$  variation from 164 to 0.14 or 1170 fold. Furthermore this variation is due wholly to differences in the ethylene data since the same values for the free energies of formation of ethyl alcohol and water were used throughout.

Comparison of these calculated values with experimentally measured ones necessitates the use of specific heat data to bridge the gap from 25° C. up to the temperatures at which the reaction becomes sufficiently rapid to permit an experimental approach to equilibrium. Since these data are rather

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meager for ethanol and ethylene, a further uncertainty is introduced. This unsatisfactory state of affairs prompted the writers to undertake further experimental work to determine directly the constant as a function of temperature.

### Previous Work

Sanders and Dodge (7) review work done prior to their investigation, both on equilibrium and on catalysts for the reaction. They studied the activity of twenty-five different catalysts for the dehydration of ethanol and presented a number of new facts about catalysts for this reaction. They investigated equilibrium in the vapor phase using a flow method and alumina catalysts, at a pressure of 70 atmospheres and a temperature of 380° C., approaching equilibrium from both sides. They made a careful study of analytical methods and were the first to prove incontrovertibly (by fractionation and by preparation of a solid derivative) that ethanol could be formed in this way. Their values for  $K_p$  varied from  $2.35 \times 10^{-3}$  to  $0.51 \times 10^{-3}$  at 380° C. with an average value of  $1.07 \times 10^{-3}$ . Stanley, Youell, and Dymock (9), using a flow method at atmospheric pressure, approached equilibrium from both sides over the temperature range 145° to 250° C. They used a silver sulfate-sulfuric acid catalyst at 145° C. and a manganese borate-phosphoric acid catalyst at the higher temperatures. The equation which they recommended as expressing their results,

$$\log_{10} K_p = \frac{2100}{T} - 6.195 \quad (1)$$

gives  $K_p = 1.06 \times 10^{-3}$  at 380° C. in almost exact agreement with Sanders and Dodge's average value (7).

Gilliland, Gunness, and Bowles (2) recently investigated the equilibrium simultaneously in both the liquid and gas phases by a static method. The catalyst was a dilute aqueous solution of sulfuric acid. Pressures were varied from 83 to 264 atmospheres and temperatures from 176° to 307° C. The following equation was stated by them to express their experimental results:

$$\Delta F^\circ = -7780 + 26.2T \quad (2)$$

which may be transformed to

$$\log_{10} K_p = \frac{1700}{T} - 5.73 \quad (3)$$

They also state that the following equation correlates all available experimental data for the vapor phase, including their own,

$$\Delta F^\circ = 26.9T - 8300 \quad (4)$$

which can be transformed to

$$\log_{10} K_p = \frac{1815}{T} - 5.890 \quad (4A)$$

The equations of Parks and Huffman (6) and of Francis and Kleinschmidt (1), based on thermodynamic data, were in poor agreement with Equation 4.

### Apparatus and Procedure for Studying Catalysts

Catalytic activity was investigated by means of the reverse reaction—namely, the dehydration of ethanol—at atmospheric pressure and 360° C., with flow rates sufficiently

high so that equilibrium was not approached. The apparatus adopted for measuring the extent of dehydration was essentially the same as that used by Huffman and Dodge (3) and Sanders and Dodge (7). Ethanol was boiled in an adiabatic boiler, so arranged that all heat of vaporization was supplied by an electric coil which allowed an easy calibration of alcohol vaporized *vs.* coil current. The vapors passed over the catalyst supported in a Pyrex glass tube which was heated in an electric resistance furnace provided with an aluminum core for smoothing out temperature variations. From the catalyst the vapors were led to a water condenser and thence to a coil condenser immersed in a mixture of solid carbon dioxide and ethanol where last traces of water and certain low boiling materials were removed. The gas was then conducted through a flowmeter (for indicating constancy of flow) and measured by water displacement. Its ethylene content was determined by absorption in fuming sulfuric acid on an Orsat apparatus.

In operating this apparatus, the two principal variables were the rate of alcohol ebullition per unit volume of catalyst and the catalyst temperature. These should be fixed so that even the best catalysts do not produce complete dehydration, in order that differentiation and comparison may be made easier. A temperature of 360° C. and an alcohol rate of 23.5 grams per hour (corresponding to a space velocity, for 5 cc. of catalyst, of 2300 volumes of gas at standard conditions per volume of catalyst per hour) satisfied this requirement.

The usual operating procedure was to bring the catalyst chamber to the desired temperature and then to start the vaporization of alcohol. This immediately produced a change in the catalyst temperature, and considerable time was required to adjust the heater to its proper setting. It was found, in the case of some catalysts, that the activity changed markedly in this period. Therefore, it was necessary to make these adjustments in as short a time as possible; at least 10 minutes were required. The run proper was then divided into 15-minute periods, the average activity being determined for each period. Thus the change of activity could be followed, and this was found to be quite noticeable in some cases.

### Catalyst Preparation

The method by which a catalyst is prepared is often of prime importance in determining its activity. In general, the best grades of chemically pure reagents were used throughout, the various steps were carried out in glassware, and the washings were made with distilled water unless otherwise specified. Precipitated catalysts were ground and screened on standard Tyler screens, only the 8 to 14 mesh size being used. Powdered catalysts were made into small pills, utilizing graphite as a binder. All catalysts were dried in an oven at about 105° C. and no additional heat treatment was given to the catalyst unless noted in Table I. The details of manufacture are as follows:

1. ALUMINA. Sixty-two grams of aluminum turnings were dissolved in a solution of 120 grams of sodium hydroxide in 600 cc. of water. The resulting solution was filtered, diluted to 6 liters, and heated to 85° C. Sulfuric acid, diluted 4 to 1 with water, was added with stirring until precipitation was complete

as indicated by red coloration of litmus paper. The precipitate was transferred to a 5-gallon (19-liter) bottle and washed seven times by decantation with distilled water. A part of it was filtered by suction and dried at 105°.

2. ALUMINA-TUNGSTIC ACID. The remainder of the settled sludge of catalyst 1 was analyzed for alumina; 500 cc. of this sludge (corresponding to 17.7 grams of alumina) were stirred and heated. During this process 0.354 gram of tungstic acid was added. It was finally evaporated to dryness in an oven at 105° C. and sized to the proper dimensions. This corresponds to 2 per cent of tungstic acid based on the anhydrous alumina.

3. ALUMINA-SULFURIC ACID. To another 500 cc. batch of sludge from catalyst 1, 0.354 gram of sulfuric acid was added, and the same treatment was given as for catalyst 2.

4. ALUMINA-POTASSIUM HYDROXIDE. Same as catalyst 2, except that 0.354 gram of potassium hydroxide was added.

5. ALUMINA-PHOSPHORIC ACID. Same as catalyst 2, except that 0.354 gram of phosphoric acid was added.

6. TUNGSTIC ACID. Twenty-five grams of powdered tungstic acid (Merck technical grade) were mixed with one per cent of its weight of graphite and pressed into pellets. Since these were a little large to feed into the catalyst tube easily, they were broken up to 8-14 mesh size.

7. TUNGSTIC ACID. Sixty grams of tungstic acid were dissolved in a solution of 26 grams of sodium hydroxide in 200 cc. of water. This solution was added to a boiling solution of 190 cc. hydrochloric acid, 190 cc. nitric acid, and 235 cc. water. It was diluted to 3 liters and washed four times by decantation. Further washing was prevented by the fact that, at this stage, the precipitate tended to become almost entirely colloidal. It was filtered by suction and dried at 105° C.

8. ALUMINA. Twenty grams of aluminum turnings were amalgamated by dipping them into a solution of mercuric chloride. The resultant amalgam was transferred to a beaker containing water, and the alumina formed was washed into a 5-gallon bottle, every few hours at first and every day thereafter, for one week. The alumina so formed was washed seven times by decantation, filtered, and dried at 105° C.

9. ALUMINA. Ninety grams of aluminum turnings were dissolved in a solution of 175 grams of sodium hydroxide in 2 liters of water. The resultant solution was filtered and diluted to 9 liters. The consequent treatment was the same as for catalyst 1, since the prime purpose was to learn how easily duplicable these catalysts were.

10. ALUMINA. One hundred and twenty-five grams of Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O were dissolved in 1.5 liters of water and heated to 85° C. Ammonium hydroxide (diluted 4 to 1) was added until precipitation was complete, as evidenced by blue coloration to litmus. It was diluted to 3 liters, washed seven times by decantation, filtered, and dried at 105° C.

11. ALUMINUM BORATE. Two hundred grams of potassium alum were dissolved in 1.5 liters of water. One hundred grams of borax were dissolved in 1.5 liters of water and the solution added to the previous one with stirring at 60° C. It was transferred to a 5-gallon bottle and washed by decantation five times. It was then filtered by suction and dried at 105° C.

TABLE I. SUMMARY OF DATA FROM CATALYST TESTS

Run No.	Catalyst No.	Catalyst Type	Per Cent Dehydration after Ethanol Flow for:						Per Cent Ethylene in Gas	Notes <sup>b</sup>
			20 min.	40 min.	60 min.	80 min.	100 min.	120 min.		
1	1	Al <sub>2</sub> O <sub>3</sub> (aluminate)	74 <sup>a</sup>	52 <sup>a</sup>	40 <sup>a</sup>	33 <sup>a</sup>	28 <sup>a</sup>	25 <sup>a</sup>	...	NA
2	2	Al <sub>2</sub> O <sub>3</sub> -WO <sub>3</sub>	90	81	71	62	53	44	98.15	...
3	6	WO <sub>3</sub> (pellets)	89	66	64	61	59	56	98.94	...
4	8	Al <sub>2</sub> O <sub>3</sub> (amalgam)	77	75	73	71	68	66	97.9	...
5	9	Al <sub>2</sub> O <sub>3</sub> (aluminate)	71	51	41	...	...	...	94.9	...
6	7	WO <sub>3</sub> (pptd.)	94 <sup>a</sup>	84 <sup>a</sup>	77 <sup>a</sup>	72 <sup>a</sup>	68 <sup>a</sup>	...	...	NA
7	11	Al <sub>2</sub> O <sub>3</sub> ·xH <sub>2</sub> O	87	81	76	73	70	68	98.57	...
8	1	Al <sub>2</sub> O <sub>3</sub> (aluminate)	83	65	67	69	71	...	97.34	A
9	1	Same	100	99	98	96	92	...	99.11	B
10	3	Al <sub>2</sub> O <sub>3</sub> -H <sub>2</sub> SO <sub>4</sub>	66	61	56	52	48	...	96.22	...
11	4	Al <sub>2</sub> O <sub>3</sub> -KOH	75	59	48	41	34	29	98.34	...
12	1	Al <sub>2</sub> O <sub>3</sub> (aluminate)	75 <sup>a</sup>	57 <sup>a</sup>	45 <sup>a</sup>	...	...	...	...	NA
13	7	WO <sub>3</sub> (pptd.)	79	74	70	66	61	57	94.6	C
14	10	Al <sub>2</sub> O <sub>3</sub> (nitrate)	17	16	...	...	...	...	96.5	...
15	10	Same	35	36	37	38	...	...	97.8	B
16	8	Al <sub>2</sub> O <sub>3</sub> (amalgam)	88	88	88	89	89	89	97.9	B
17	11	Al <sub>2</sub> O <sub>3</sub> ·xH <sub>2</sub> O	56	52	49	48	...	...	98.4	B
19	12	Al <sub>2</sub> O <sub>3</sub> (aluminate)	61	62	63	63	64	65	97.5	B
20	12	Same	77	79	81	83	85	87	97.95	D
21	5	Al <sub>2</sub> O <sub>3</sub> -H <sub>3</sub> PO <sub>4</sub>	92	72	56	45	38	...	97.45	...
22	12	Al <sub>2</sub> O <sub>3</sub> (aluminate)	75	73	69	67	...	...	96.5	E
23	12	Same	36 <sup>a</sup>	...	...	...	...	...	...	NA

<sup>a</sup> Assumes 100% ethylene in exit gas.

<sup>b</sup> Notes: NA, gas not analyzed; A, used in run 1 and reactivated at 500° C. with air for 2 hours; B, preactivated at 500° C. with air for 2 hours; C, preactivated at 450° C. with a 2 to 1 H<sub>2</sub>-CO mixture for 2 hours; D, used in equilibrium runs 13, 14, and 15, reactivated for 2 hours at 500° C. with air, and used in equilibrium runs 17-23; E, same as B but for 4 hours.

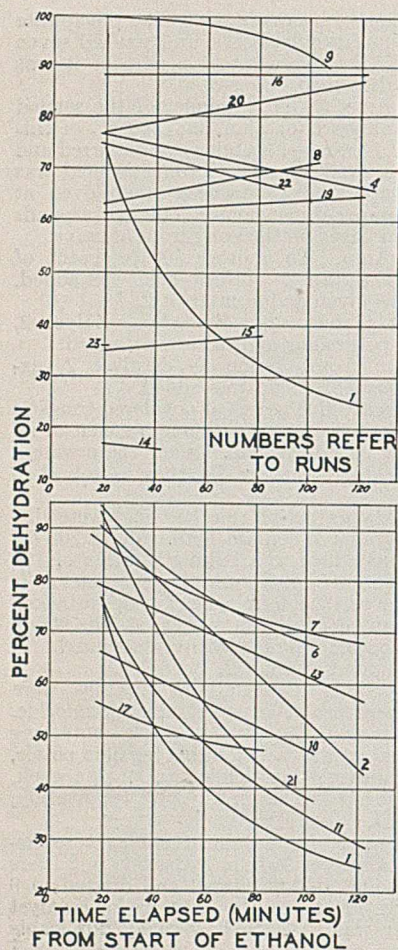


FIGURE 1. COMPARISON OF CATALYSTS FOR DEHYDRATION OF ETHANOL

carbonate, 12.4 grams of boric acid, and 47 cc. of 85 per cent phosphoric acid were intimately mixed with about 100 cc. of water. The mixture was evaporated with stirring and then baked in an oven for 4 hours at 240° C. The resulting material was then ground and screened to 8-14 mesh size. This has the approximate molecular formula  $MnO \cdot BO \cdot 3\frac{1}{2}H_2PO_4$  and was made to conform to a catalyst used by Stanley, Youell, and Dymock (9).

16. SILVER SULFATE-SULFURIC ACID. Sixty-five cubic centimeters of sulfuric acid were added to 35 cc. of water, and 5 grams of silver sulfate were dissolved in the acid solution with heating. In this solution 8-14 mesh pumice was soaked for 3 hours, filtered on glass wool, and dried at 105° C. This also was an attempt to duplicate a catalyst suggested by Stanley, Youell, and Dymock (9).

17. ALUMINUM SULFATE. Fifty grams of ammonia alum were calcined slowly at 400° C. for 20 minutes. The material was then removed, and the hardened bubbles formed by the calcination were broken. It was returned for 10 minutes more. It was then removed, powdered, and heated again for 30 minutes at a slightly lower temperature. After cooling, it was mixed with 2 per cent of its weight of graphite and pressed into pellets.

18. CADMIUM PHOSPHATE. One hundred and fifty-four grams of  $Cd(NO_3)_2 \cdot 4H_2O$  were dissolved in water and precipitated with sodium hydroxide. The cadmium oxide was washed by decantation four times, made up to a slurry of 1200 cc., stirred, and heated. Sixty-four grams of phosphoric acid were added, and heating was continued until most of the water had evaporated. It was then transferred to an oven where final evaporation to dryness took place at 130° C. This was an attempt to duplicate a catalyst suggested in a patent granted to the Imperial Chemical Industries (4).

19. ALUMINA. Four hundred and ten grams of powdered aluminum were dissolved in a solution of 820 grams of sodium hydroxide in 6 liters of water. The resulting solution was filtered, diluted to 45 liters, heated to 85° C. in an enamel-lined steam kettle, and precipitated with one to one sulfuric acid until litmus turned red. The resultant mixture was diluted to 50 gallons and washed seven times by decantation with tap water. It was filtered by suction and dried at 105° C.

12. ALUMINA. Three hundred and ten grams of aluminum turnings were dissolved in a solution of 600 grams sodium hydroxide in 4 liters of water. The resulting solution was filtered, and the filtrate diluted to 45 liters and heated to 85° C. in an enamel-lined steam kettle. It was precipitated with a 4 to 1 solution of sulfuric acid until litmus turned red, and the sludge was diluted to 50 gallons (189 liters) in a barrel. The latter was washed seven times by decantation with tap water, filtered by suction, and dried at 105° C.

13. ALUMINA AEROGEL. This catalyst was kindly supplied by S. S. Kistler of the Norton Company.

14. ALCOA ACTIVATED ALUMINA. This catalyst is a commercial adsorbent marketed by the Aluminum Company of America.

15. MANGANOUS OXIDE - BORIC ANHYDRIDE - PHOSPHORIC ACID. Twenty-three grams of manganous carbonate, 12.4 grams of boric acid, and 47 cc. of 85 per cent phosphoric acid were intimately mixed with about 100 cc. of water.

20. ALUMINUM BORATE. Twelve hundred grams of potassium alum were dissolved in 20 liters of water, diluted to 45 liters, and heated to 85° C. in an enamel-lined steam kettle. To this a solution of 650 grams of borax in 12 liters of water was added until litmus turned faintly blue. It was transferred to a 50-gallon barrel and washed seven times by decantation with tap water, filtered by suction, and dried at 105° C.

21. TUNGSTIC ACID. Five hundred grams of this material were pressed into pellets in the same way as catalyst 6.

## Data and Conclusions

The criterion of catalyst activity was the extent of dehydration or, more specifically, the percentage of ethanol passing over the catalyst which undergoes decomposition to ethylene. This will be denoted by the term "per cent dehydration." It is also important to determine the specificity of the catalyst for this particular reaction and this may be judged by the ethylene content of the gases produced. With all the catalysts studied, the ethylene content was 94 per cent or higher, indicating that dehydration was the predominating reaction.

Since it was almost impossible to obtain exactly the same prerun period for each test, the variation of catalyst activity with time was plotted and the results given in Table I were read from the curves. The most significant results are also presented graphically in Figure 1, using the smoothed data.

Comparisons of runs 1 and 12 made on the same catalyst and runs 1 and 5 made on catalysts prepared in the same way indicate that both the methods of catalyst preparation and the testing procedure are reasonably reproducible. The following conclusions may also be drawn from the data presented:

(1) All of the catalysts, if not given any special activation treatment, showed a continued diminution of activity with time during use. This behavior was more pronounced with the alumina than with the tungstic oxide catalysts and there were differences in the alumina catalysts in this respect, depending on the method of preparation (for example, runs 1-4, 6, 7).

(2) Treatment of an alumina catalyst with air for a short period at a temperature well above its normal operating temperature (500° C. used in most cases) not only increased the initial activity but stabilized the catalyst so that decrease in activity with use was either prevented entirely or greatly minimized (compare runs 1, 8, and 9; 14 and 15; 4 and 16).

(3) Addition of a small percentage (about 2 per cent) of tungstic oxide or phosphoric acid to an alumina catalyst increased its initial activity somewhat but had no effect on the stability. A small amount of sulfuric acid reduced initial activity but lessened the rate of decrease of activity, whereas a small percentage of potassium hydroxide was without significant effect on either property (compare runs 1 and 2; 1 and 10; 1 and 11; 1 and 21).

(4) Alumina made by ammonium hydroxide precipitation was a less active catalyst than alumina made either from aluminate or from aluminum amalgam (confirms results of Sanders and Dodge, 7). Heat treatment at 500° C. improved its activity greatly but still left it inferior to the other two (compare runs 1 and 14; 4 and 15).

(5) An aluminum borate catalyst is somewhat more active initially than the best alumina catalysts, but heat treatment at 500° C. reduced its activity and did not make it as stable as the pure alumina catalysts (runs 7 and 17).

(6) Tungstic oxide is more active initially and more stable than the best unactivated alumina catalysts, but treatment with a reducing gas at 450° C. reduced the activity and did not stabilize the catalyst. The lower activity of catalyst 6 as compared to 7 was probably due to the fact that the tungstic oxide was simply a technical grade used without further treatment whereas catalyst 7 had been precipitated (compare runs 4, 6, and 13).

In view of the large number of variables and the small number of tests, these conclusions are tentative but should prove a useful guide to anyone who is starting work with catalysts of this type.

The results of a few other tests were poor or negative and are not recorded in Table I, but a record of them may prove useful to others. An alumina aerogel (catalyst 13) gave only 8 per cent dehydration and a gas containing only 88 per cent ethylene. Catalyst 15, a manganese borate-phosphate catalyst made according to the directions of Stanley, Youell, and Dymock (9), was active initially but soon became wholly inactive. Distinct tests for phosphate in the liquid product indicated that the loss of activity was probably due to the volatilization of phosphoric acid. However, this catalyst was used successfully by Stanley, Youell, and Dymock at a temperature at least 100° C. less than that of the present experiment, which may account for the difference in behavior.

Cadmium phosphate catalyst 18, made according to directions in a patent (4), was wholly inactive. Commercial activated alumina (Alcoa) exhibited slight activity, and aluminum sulfate, prepared as directed by Senderens (8), was of low activity, giving 15 per cent dehydration at 360° C.

### Equilibrium Measurements

As mentioned at the beginning, the chief aim of this work was the evaluation of the equilibrium constant. For this purpose an apparatus had to be designed and a procedure chosen so that the amounts of reactants and products at equilibrium could be measured. There are two general methods of accomplishing this end—a static method and a dynamic one; in this work the latter was adopted. Ethylene and water vapor were passed over a catalyst at an elevated temperature under moderate pressure; the liquid products were condensed, weighed, and analyzed; and the gaseous products were metered and analyzed. Knowing the total pressure and the amounts of ethylene, ethanol, and water in the product from the reaction,  $K_p$  can be calculated by the expression:

$$K_p = \frac{x_{C_2H_5OH}}{x_{C_2H_4} \cdot x_{H_2O} \cdot P}$$

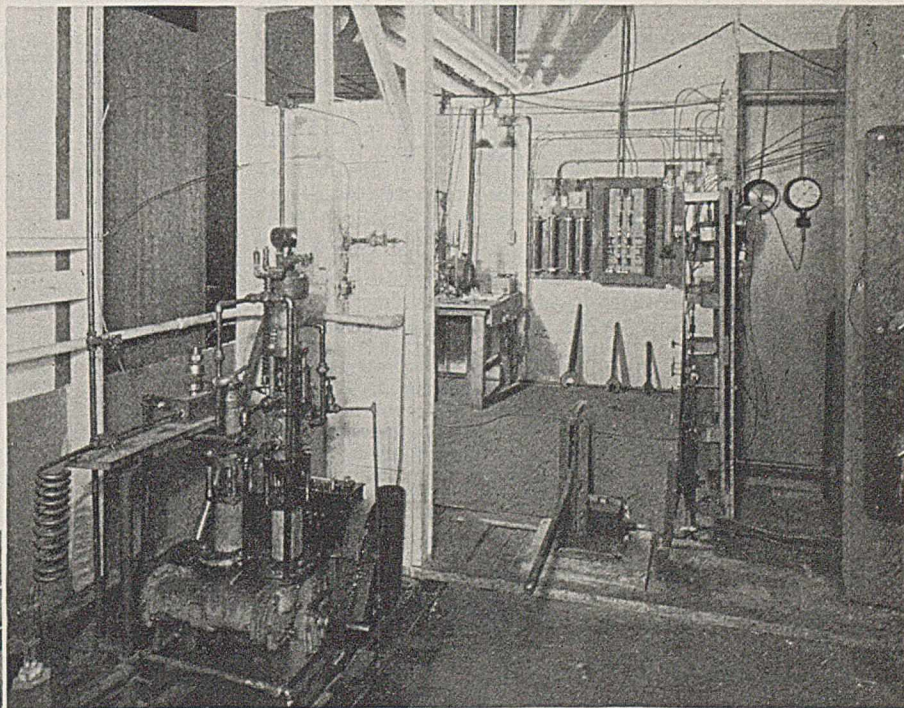
where  $x$  = mole fraction of each component

$P$  = total pressure

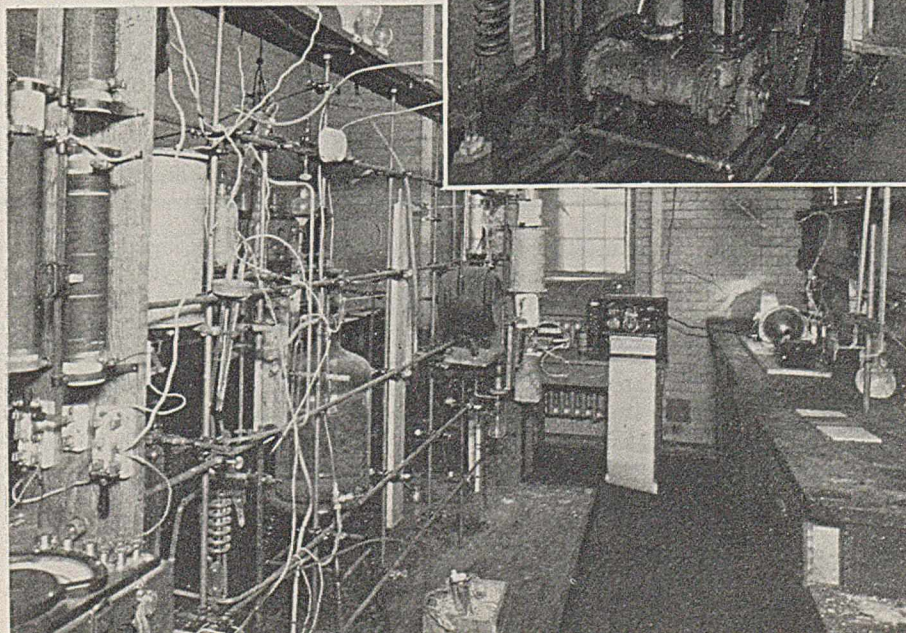
Two methods were used to indicate that an approach to true equilibrium was being attained. The first was to vary the space velocity and the second was to add ethanol to the reactants in excess of the approximate equilibrium amount so that the direction of the reaction was reversed. If the same value for  $K_p$  is obtained, confidence that equilibrium has been reached is justified.

Another equally important consideration essential to the accuracy of results is the elimination of appreciable side reactions. Provision has been made in the analytical scheme to determine the amounts of ethyl acetate, acetic acid, and acetaldehyde so formed and to remove any ether from interference with the ethanol analysis. All results (with the exception of those obtained with tungstic acid catalysts) show that these materials are formed in negligible amounts. There is, however, one other side reaction which is very troublesome—namely, the polymerization of ethylene. This reaction consumes ethylene, thus continually disturbing the equilibrium sought, and the polymer so formed interferes with determining water in the product by difference. It cannot be analyzed by any simple means, and it is of such complex structure that estimation of its molecular weight is impractical. Therefore, in order to make equilibrium results of value, it is absolutely essential to avoid this side reaction.

The conditions chosen for the investigation were temperatures of 320° to 380° C., pressures of 7 to 11 atmospheres, space velocities of 3 to 75, and ethylene-steam ratios of 0.25 to 9. Temperature was limited on the low side by the activity of the catalysts and on the high side by side reactions. Although the yield of ethanol increases nearly in proportion



(Above)  
CORNER OF HIGH-PRESSURE  
LABORATORY



(Left)  
APPARATUS FOR STUDYING  
CATALYTIC GAS REACTIONS

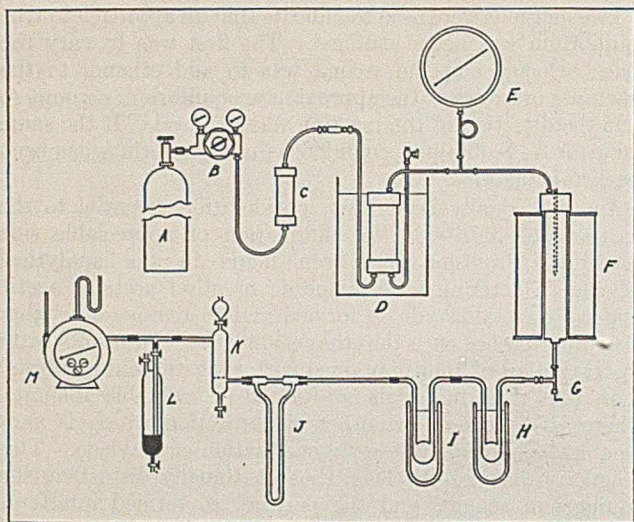


FIGURE 2. DIAGRAM OF EQUILIBRIUM APPARATUS

to the pressure, this was kept at a relatively low value to minimize polymerization and to simplify the apparatus. Space velocity and ethylene-steam ratio were varied within wide limits, mainly because it was not possible to predict in advance the best conditions to use and because the steam ratio was not under close control.

### Apparatus and Procedure

The moderate pressure permitted the use of a simple apparatus constructed of ordinary pipe and fittings and modeled after that used by Newton and Dodge (5) in their work on the methanol equilibrium. The complete assembly is shown in Figure 2:

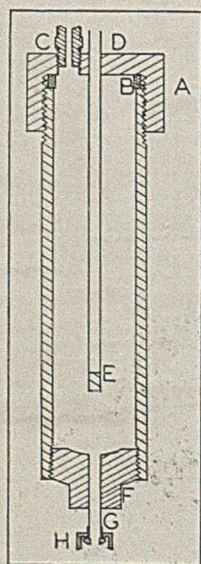


FIGURE 3. CATALYST REACTOR

- A = pipe cap
- B = copper gasket
- C = union
- D = thermocouple well
- E = silver-solder plug
- F = pipe plug
- G = gas outlet tube
- H = union

expansion valve *G* are provided with radiant electric heaters to prevent trouble from condensation of material from the gas as a result of the cooling due to expansion. The reactor, holding approximately 300 cc. of catalyst, is made from extra heavy steel pipe and is unlined. Temperature was measured by a

thermocouple inserted in a steel well which projected into the catalyst bed and was controlled by manual adjustment of the current.

The equilibrium runs varied in length from 2 to 18 hours and were preceded by a prerun period of 5 to 7 hours which was necessary for the adjustment of the operating conditions to the values desired. During this period, traps *H* and *I* (Figure 2) were bypassed. At the completion of a run, these traps were removed and weighed to determine total material condensed, and the contents combined for analysis.

Analysis of the gas sample was conducted on an Orsat apparatus using a mercury-sealed compensated buret, and absorbing the ethylene in fuming sulfuric acid. Carbon dioxide, oxygen, carbon monoxide, and in some cases hydrogen and hydrocarbons, were also determined. The liquid condensate, freed from any nonaqueous layer, was analyzed for ethanol and water by the method of Sanders and Dodge (?).

### Discussion of Results

The summarized results from twenty-nine runs are presented in Table II. The results are separated into three groups to facilitate discussion. The runs of the first group, arranged in order of increasing ratio of oil to ethylene, give  $K_p$  values which are believed to be too low. This is thought to be partly due to the relatively large amounts of oil formed as a result of ethylene polymerization. Not only does this lead to errors in the determination of the water by difference and in the estimation of the molecular weight of the gas, but it means that the equilibrium desired is being continually disturbed by a side reaction. If we rule out runs 6, 7, 11, 12, and 16 on the basis that the catalysts (19 and 21) used had not been thoroughly studied, and that side reactions other

TABLE II. EQUILIBRIUM RESULTS<sup>a</sup>

Run No.	Saturator Temp. ° C.	Catalyst Temp. ° C.	Pressure Atm.	Space Velocity <sup>b</sup>	Ethylene-Steam Ratio Moles/mole	Oil per Mole C <sub>2</sub> H <sub>4</sub> Grams	$K_p \times 10^4$
7	114	379	11.81	23.8	4.95	0.65	7.04
6	114	382	11.31	9.12	2.67	1.01	6.92
16	114	374	11.25	3.36	3.78	1.55	4.10
18 <sup>c</sup>	114	378	11.1	7.55	8.95	1.89	9.45
10 <sup>c</sup>	114	377	11.13	11.71	3.35	2.19	7.24
8	114	374	11.12	18.1	3.09	2.19	8.37
11	114	375	11.24	18.4	4.46	2.49	4.46
19 <sup>c</sup>	114	376	11.08	9.10	6.70	2.58	10.71
14 <sup>c</sup>	114	377	11.03	12.8	5.51	2.72	10.35
9 <sup>c</sup>	114	378	11.13	10.72	3.28	2.79	6.45
15	114	376	10.98	8.06	3.65	4.37	7.51
17 <sup>c</sup>	114	380	11.25	10.33	5.15	4.62	4.61
12	114	379	11.24	2.85	3.35	6.77	1.30
24	153	378	7.32	4.50	1.57	0.59	12.6
23 <sup>c</sup>	148	379	7.50	6.50	4.50	1.35	10.0
20	146	381	7.30	9.11	1.24	0.68	13.68
21	146	378	7.40	9.70	1.43	0.0	12.68
22 <sup>c</sup>	148	380	7.87	10.34	1.72	0.37	12.33
25 <sup>c</sup>	154	378	6.71	10.80	2.14	0.32	12.31
26	163	378	7.17	11.0	0.69	0.0	12.62
28 <sup>c</sup>	163	378	7.18	67.6	0.42	0.0	13.80
27	163	376	7.31	74.0	0.38	0.0	10.84
36 <sup>c</sup>	163	320	6.80	5.20	1.04	none	18.44
35	163	321	6.90	17.20	0.32	none	18.95
34 <sup>c</sup>	163	348	7.46	9.00	1.26	none	15.80
31	163	350	7.24	8.73	0.87	none	14.40
32	163	350	8.13	20.5	2.15	none	22.00
30 <sup>c</sup>	163	351	7.04	21.3	0.27	none	14.90
33	163	351	7.25	8.10	6.10	none	14.50

<sup>a</sup> Catalysts were used as follows: runs 6 and 7, catalyst 19; runs 8, 9, 10, 13, 14, 15, 17-36, catalyst 12; runs 11, 12, 16, catalyst 21. Catalysts were given high-temperature activation treatment in all cases except runs 6 and 7.

<sup>b</sup> Space velocity = liters of off-gas at standard conditions per liter of catalyst volume per hour.

<sup>c</sup> Decomposition run.

than ethylene polymerization might be occurring, a plot of  $K_p$  vs. grams of polymer per mole of ethylene for fifteen runs shows a rough correlation between them;  $K_p$  increases as the polymer decreases. On the basis of these facts, the  $K_p$  values of this first group of runs will be ignored in arriving at the best value for this constant. Nevertheless these runs are interesting from the standpoint of showing how much polymerization can occur at these relatively low temperatures and pressures.



Another observation worthy of note is the fact that the liquid product from the three runs using the tungstic oxide catalyst contained more acetic acid than ethanol. This behavior was thought to be due to the reduction of the catalyst by the ethanol formed, although this catalyst had been treated with a mixture of carbon monoxide and hydrogen for 2 hours at 500° C.

The second group of runs was made at the same temperature but with a reduced pressure and a smaller ethylene-steam ratio. This led to a considerable reduction and, in some cases, to practically complete elimination of the polymer with resulting higher  $K_p$  values. Omitting run 23 because of the relatively large amount of polymer formed, the average  $K_p$  from all the other runs of this group is  $12.6 \times 10^{-4}$ . Supporting evidence that this is very close to the true value may be summarized as follows:

1. Runs 22 and 25 were in the decomposition direction; runs 20, 21, 24, and 26 were in synthesis.

2. The space velocity varied from 4.5 in run 24 to 11.0 in run 26 (almost threefold variation) without appreciable effect on  $K_p$ .

3. Run 27, with a space velocity of 74, in the synthesis direction gave a value of 10.84; run 28, with a space velocity of 68 in the decomposition direction, gave a value of 13.8. It is apparent that  $K_p$  must lie between these values; in fact, the average is very close to the average for the whole group.

4. The maximum amount of oil formed in any of these runs was 0.6 gram per mole of ethylene or about 2 per cent of the weight of the ethylene.

5. At 350° C.,  $K_p$  rises to  $14.9 \times 10^{-4}$ , a higher value at a lower temperature, which is to be expected.

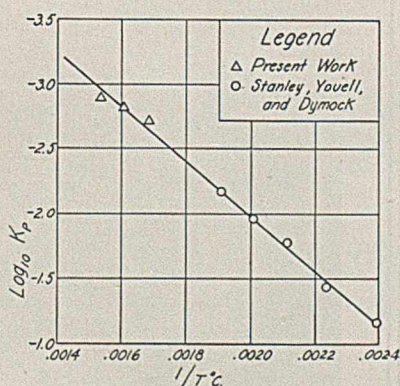


FIGURE 4. CORRELATION OF EQUILIBRIUM RESULTS WITH THOSE OF STANLEY, YOUELL, AND DYMOCK

The third group includes runs made at lower temperatures. The average  $K_p$  values (omitting run 32 which is entirely out of line with the others) are  $14.9 \times 10^{-4}$  at 350° C. and  $18.7 \times 10^{-4}$  at 320° C. Because of the small number of runs made, the results at 320° C. cannot be given as much weight as the values for 350° and 378°. It is worthy of note that ethylene polymerization was negligible at these lower temperatures even when the ethylene-steam ratio was relatively high. Since the pressures were not far from atmospheric, these  $K_p$  values may be assumed equal to  $K_p$  (value at low pressure) without introducing appreciable error.

Proof of the fact that equilibrium was actually approached from the decomposition side, when dilute ethanol was used in the saturator, was obtained by one such run when no catalyst was present. In this case the apparent value of  $K_p$  was several times the highest value found in any equilibrium run.

These results cover too narrow a temperature range and are too uncertain at the lowest temperature to permit any deduc-

tions as to the change of  $K_p$  with temperature. They can, however, be combined with the lower temperature results of Stanley, Youell, and Dymock, as Figure 4 shows. The equation of the best straight line through these points is:

$$\log_{10} K_p = \frac{2132}{T} - 6.241 \quad (5)$$

which agrees rather closely with the equation used by Stanley, Youell, and Dymock to represent their own results. Putting it in the form of a free-energy equation, we have:

$$\Delta F^\circ = 28.60T - 9740 \quad (6)$$

Since it is believed that the  $K_p$  value for 320° C. is less accurate than the values for the two higher temperatures used in this investigation, another equation has been derived, using the two points for the higher temperatures from the present investigation, combined with the several points of Stanley, Youell, and Dymock. The resulting equations are:

$$\log_{10} K_p = \frac{2100}{T} - 6.170 \quad (7)$$

$$\Delta F^\circ = 28.20T - 9600 \quad (8)$$

Equations 7 and 8 are recommended in preference to 5 and 6.

TABLE III. COMPARISON OF  $K_p$  VALUES

$T, ^\circ \text{K.}$	$K_p \times 10^4$			
	Equation 7	Equation 1	Equation 3	Equation 4A
400	120	114	33	44.6
500	10.7	10.1	4.7	5.5
600	2.14	2.02	1.27	1.37
700	0.68	0.64	0.50	0.50

The agreement between Equations 1 and 7 and the two equations given by Gilliland, Gunness, and Bowles—is not as good as might be wished (Table III). Their equation to represent all published experiments is not greatly different from their other equation and does not give much weight to the results of Stanley, Youell, and Dymock. Part of the disagreement may be due to the uncertainty in the pressure correction which Gilliland and co-workers had to make to obtain the standard free-energy change. This was done by means of the assumption of an ideal solution coupled with the published fugacity charts for hydrocarbons. Since, under the experimental conditions, ethanol is below its critical temperature and above its critical pressure, the assumption of an ideal solution is probably not very good and the estimation of the fugacity involves an extrapolation into an unstable region where ethanol vapor cannot normally exist.

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RECEIVED May 27, 1936. Based on a dissertation presented by R. H. Bliss in June, 1935, to the faculty of the Graduate School of Yale University, in candidacy for the degree of doctor of philosophy.

# Nitration of Purified Wood Fiber

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Brown Company, Berlin, N. H.

Coniferous wood pulp refined by methods which greatly reduce its content of resinous and other coloring matter and which raise the alpha-cellulose content has been successfully nitrated on a commercial scale to yield nitrocellulose suitable for conversion into the superior grades of plastics, lacquers, etc.

The refined wood pulp has been nitrated as tissue, as shreds resembling cotton linters, and as dryer board. Of importance are certain details of process in the conversion of pulp into these different forms, and of nitration.

A method has been developed for converting pretreated wood fiber into so-called half-second nitrocellulose without recourse to the usual hazardous step of digesting nitrocellulose under pressure. The yields are high and the quality excellent.

of solutions of guncotton alone or admixed with gums and resins as protective coatings (33), but also had already made headway in the preparation of solid masses from nitrated cellulose (79). In the same year Andemars was granted a patent on the manufacture of imitation silk from a combination of nitrated mulberry branches and rubber (2), a sort of "sympathetic magic." Patents underlying modern practice in the manufacture of celluloid were granted to the Hyatt brothers in 1869-70 (26). The development of gelatin dynamite followed Alfred Nobel's discovery in 1875 that a relatively small quantity of nitrocellulose will gelatinize nitroglycerine when dissolved in it (75, 83). In 1884 Chardonnet disclosed his process of squirting through tiny orifices fine streams of nitrocellulose dissolved in ether-alcohol and of producing, upon evaporation of the solvent, delicate silklike threads of the nitrate (12). About this time modern smokeless military powder, prepared by colloidizing nitrocellulose and converting it into strips, was invented by the Frenchman Vieille (75, 82), stimulating anew the efforts of nations

AIRPLANE VIEW OF

SINCE Braconnot (8) in 1832 and Pelouze (35) in 1838 treated cellulose with nitric acid, and Schönbein (45, 75) in 1845-6 recognized the technological importance of nitrated cellulose, an enormous volume of research has been conducted throughout the world to uncover the mechanism of the reaction, to explore and to control the properties of the nitrocellulose, and to take advantage of the extraordinary and valuable characteristics of the product (67, 76, 77). The destructive nature of the novel cellulosic compound first aroused general interest; nations vied with one another in their efforts to become expert in the manufacture and adaptation for military purposes of the remarkable, powerful explosive which leaves no telltale engulfing smudge on the horizon. All Europe rushed into large-scale production with only a meager understanding of the temper of the new genie. A disastrous explosion wrecked the first nitrocellulose plant in England as early as 1847; this was soon followed by devastating explosions in France. Similar experiences were suffered by Russia, Austria, Prussia (78) and, in consequence, nitrated cellulose fell into bad repute until Abel in 1866-7 showed that its stability is vastly improved by pulping or cutting the nitrated fiber in the presence of water, as in a paper-maker's beater, so as to facilitate extraction of residual acid from the fiber canal (1, 75).

Other uses for nitrated cellulose were quickly developed. Maynard and Bigelow independently suggested solutions in ether-alcohol for dressing wounds (80). One wonders that comment is not more frequent on the irony of the sequence: the first use, destruction; the second, healing. Then followed the suggestion of le Gray in 1850 and of Archer in 1851 (81) for the use of collodion—i. e., the ether-alcohol solution—in photography. In 1855 Parkes not only proposed the use



to develop satisfactory smokeless propellants. To Field (20) is generally credited the introduction in 1890 of the modern type of lacquer in which nitrocellulose and resins are dissolved in solvents of graded volatility (68). The development of these ideas and the evolution of many others have steadily continued, until today the manufacture of nitrocellulose and its conversion into explosives, films, lacquers, celluloid, artificial leather, shoe cement, and the like, constitute a stout branch of industry.

The scope of this paper does not permit the presentation of statistics showing that in the United States alone the production of nitrated cellulose has run into more than a thousand tons every month, with a market value of more than a million dollars, which rapidly expands as the raw material is converted into numerous end products. True, viscose rayon has displaced Chardonnet's silk; cellulose acetate is competing with the nitrate in the manufacture of films and safety glass; and the new condensation and polymerization resins are crowding celluloid in many fields. The nitrocellulose industry, however, continues to grow, urged on by intense economic pressure constantly to seek and to find new and wider commercial outlets. The improvements in nitrate lacquers and the expansion in their use since the World War (10, 34), and the spread in the adoption of safety glass (71) are truly phenomenal.

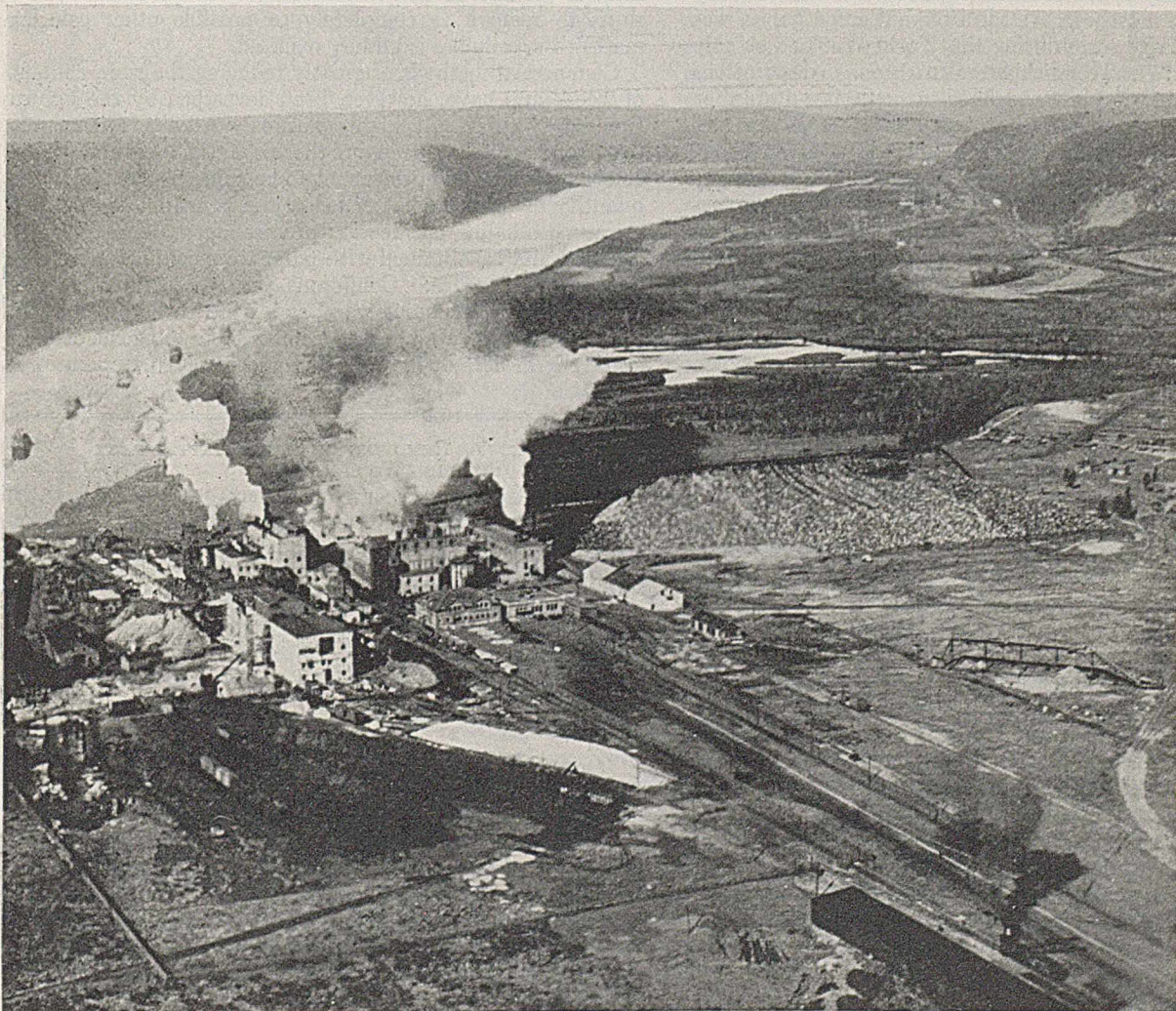
Cotton for more than one reason, constitutes by far the chief source of cellulose used in the manufacture of nitrocellulose. It is the purest form of cellulose occurring in nature

in abundance; as picked it contains about 90 per cent cellulose relatively easy to free almost completely from impurities (22). It has been nitrated in many forms—as skeins of Sea Island cotton in the early days of the manufacture of the new explosive, as unspun cotton waste, as rag or cotton linter paper, and as linters. Cotton is the cellulosic raw material with which the nitrating industry as a whole is most familiar and in which it has had most confidence.

Wood fiber, however, has been studied intensively as a source of cellulose for nitration, particularly by the nations whose supply of cotton is not infallible. In 1865 Schultze, an officer in the Prussian artillery, published a brochure on the manufacture of gunpowder by nitrating flakes of wood previously cooked in soda solution, then washed and bleached (19). The Schultze Gunpowder Company of England manufactured shotgun powder from nitrated wood for over fifty years, starting in 1868 (75).

A comparison between cotton and wood pulp was made in 1912 by Tedesco; he advanced data to show that wood cellulose yields a nitrate dangerously less stable than gun cotton (69). Tedesco worked with sulfite pulp purified by treatment with calcium hypochlorite solution, followed by leaching with dilute caustic soda solution and extraction with alcohol. The fiber thus purified was dried, disintegrated into fine shreds, and finally nitrated. The procedures followed in the purification and in the shredding of the wood pulp had been developed twenty-two years earlier by the famous Waldhof Zellstoff Fabrik specifically for the manufacture of

BROWN COMPANY PULP MILLS, LA TUQUE, P. Q., CANADA



stable nitrocellulose powder (85). Nitzelnadel, on the other hand, concluded from his work, which was practically contemporaneous with Tedesco's, that wood pulp nitrocellulose intended for military use is well above official requirements in stability (30, 34). About two years later, in fateful 1914, Schwalbe and Schrimppf, in a preliminary report of an extensive investigation into the suitability of commercial wood pulps for the manufacture of smokeless powder, also concluded that wood cellulose yields a satisfactorily stable product (66). Schrimppf later made a final report in which he gave details of procedure and criticized both Tedesco and Nitzelnadel for having deviated in some essential points from customary nitration practice (47).

TABLE I. EFFECT OF REMOVING RESINOUS MATTER FROM SULFITE FIBER<sup>a</sup>

	Sample 1	Sample 2
Resins, %	0.56	0.04
$\alpha$ -Cellulose, %	87.6	87.9
Copper No.	2.12	1.72
Pentosans, %	3.56	3.95
Color of pulp	110	112
Ash, %	0.10	0.11
Soly. in 7.14% NaOH soln., %	10.6	11.6
Cuprammonium viscosity	6.1	7.0
Color of nitrocellulose solution	60	25

<sup>a</sup> Nitrated in the form of 0.25-inch squares of 30-pound paper. The procedures used in laboratory nitrations are described at the close of the paper. All chemical usages, yields, etc., are expressed on a bone-dry basis.

In 1918 the du Pont Company successfully manufactured 100,000 pounds of nitrocellulose from a mixture of equal parts of wood pulp and cotton without loss in rate of production or in quality of the finished powder (76). In Germany wood cellulose, mostly in the form of thin crepe paper, was nitrated on a large scale during the World War and shortly thereafter (39, 75). Technical literature is rich in descriptions of methods of purifying wood fiber to make it suitable for nitration and in dissertations on wood cellulose as raw material for the manufacture of nitrocellulose (6, 11, 13, 16, 17, 18, 28, 30, 32, 39, 47, 49, 64, 65, 66, 69, 72, 74), but ordinarily very little purified wood cellulose has been used in the preparation of cannon powder or high-grade industrial nitrocelluloses. As Woodbridge explains, the chemical stability of smokeless powder during actual storage has been a matter of great concern, especially since too little has been known of the factors affecting stability; hence government officials have been greatly averse to a change from cotton, which was early adopted, to any other source of cellulose in the preparation of gunpowder (75). The same was true, to a certain extent, with regard to the attitude of the manufacturers of celluloid, lacquers, films, etc., but in this case undoubtedly the repeated failures of the early workers in the field to produce a suitable pulp in the proper physical form did much to discredit wood cellulose.

A study of the nitration of wood pulp for conversion into plastics and lacquers was undertaken by the Brown Company in 1923 as part of a program for developing markets for highly refined wood fiber (23, 42). It was felt that the opportunities for commercial success were greater in the nonexplosive fields, particularly during peacetime, because of the lack of long-time stability records of military powders prepared from wood pulp and stored under varying conditions (75). Methods were evolved for manufacturing pulps especially suited for conversion into the highest grades of commercial nitrates; and methods of nitration were devised particularly suited to the pulps. Experience with these fibers in the United States and abroad demonstrates fairly conclusively that

properly refined and suitably prepared wood pulp can compete in quality with cotton or rag paper and with cotton linters when cleanliness, clarity, substantial freedom from coloring matter, and uniformity in quality are important considerations in the finished products, and where steadiness in the price of the cellulosic raw material is appreciated.

### Purification of Wood Pulp for Nitration

Pulp for nitration purposes, like cotton, must be comparatively free from coloring matter if it is to prove satisfactory for the manufacture of high-grade colorless or delicately tinted nitrocellulose products. Photographic films and the celluloid layer in safety glass are ordinarily required to be practically colorless, and celluloid toilet ware must frequently be made to match a color standard. Although a slight brownish discoloration can sometimes be masked through the skillful use of pigments and dyes, normal variations in the degree of discoloration caused by improper purification of the cellulose would make color control a costly and arduous procedure. In this respect pulps purified by methods such as are suggested by Opfermann and Friedmann (32), Schwalbe (64), Wilstätter and Clemm (74), Drewsen (17), and Wells and Edwardes (72) are unsatisfactory and ordinarily cannot compete with modern purified linters, for, with all wood or wood pulps hitherto commercially available, the methods lead to nitrated products of relatively poor color. These pulp-refining processes generally involve the step of recocking or steeping the fiber in an alkaline liquor, in some instances after a preliminary oxidation of the impurities. Invariably, however, too high a residue of color-generating resinous matter survives. Furthermore, if the fiber is bleached thoroughly in the usual manner so as to remove as completely as possible other coloring matter, the cellulose is unduly oxidized.

Commercial methods of greatly reducing the resin content of wood pulp have, however, been developed by the Brown Company; as a result, highly purified wood fiber remarkably free from resin has been on the market for several years. Illustrative of the improvement to be gained by reducing the quantity of resinous matter below the point obtainable with the usual alkaline purification process are the data given in Tables I and II, obtained with pulps from coniferous wood—for example, spruce. Coniferous wood is of greater fiber length than is deciduous wood and is hence better adapted to the production of pulp capable of withstanding the disintegrating influences of the nitrating and associated operations.

TABLE II. EFFECT OF REMOVING RESINOUS MATTER FROM PURIFIED WOOD FIBER

	Normally Purified Wood Fiber		Normal Nitrating Grade Cotton Linters	Highly Purified Wood Fiber	
	Normal resin content	Low resin content		Sample 3	Sample 4
Resins, %	0.12	0.02	0.04-0.14	0.16	0.06
$\alpha$ -Cellulose, %	92.7	92.9	96-98	95.7	95.9
Color of pulp	108	112	...	109	110
Form in which nitrated	0.25-in. squares of 30-lb. paper	0.25-in. squares of 30-lb. paper	In bulk	0.25-in. squares of 30-lb. paper	0.25-in. squares of 30-lb. paper
Nitrating yield, %	151	150	147-153	152	152
Color of nitrocellulose soln.	34	22	22-50	40	22

Despite the fact that resinous matter may be almost completely eliminated by one method or another, the pulp must be thoroughly bleached to yield nitrates low in color content. The final bleaching should be carefully executed, however, for alkali-refined pulps are comparatively sensitive to the action of oxidizing agents, and unless special precautions are taken, high whiteness will be had only with a lowered

alpha-cellulose content and an increased copper number. Whether the oxidation of an alkali-purified pulp is really detrimental depends upon the extent of the oxidation and upon the type of nitrate desired. In this connection, a search through the literature dealing with nitration of cellulose from different sources is not altogether satisfying, for the number of important factors involved is considerable, including the physical condition of the cellulose, the composition of the acids, the type of nitrating apparatus, the procedure followed in stabilizing, the degree of nitrification desired, the use to which the nitrocellulose is to be put, the translation of laboratory results into terms of mill practice, and many other considerations (3, 5, 6, 16, 21, 31, 42, 46, 47, 72, for example). The impression is gathered, however, that for optimum results, embracing the factors of yield, ease of stabilization, and acid economy, the cellulosic raw material should ordinarily be as nearly free as possible from impurities and from hydrolyzed or oxidized cellulose. Consequently, in preparing pulps for conversion into high-grade nitrates relatively free from coloring matter, the attainment of whiteness with a minimum oxidation of the cellulose is highly desirable.

If the refined wood pulp is properly bleached, it will be very white, yet high in alpha-cellulose content, low in copper number, and relatively stable in whiteness when heated over long periods of time, and will yield nitrocelluloses low in content of coloring matter. Typical examples are given in Table III.

TABLE III. IMPROVEMENT TO BE GAINED BY BLEACHING ALKALI-REFINED PULP<sup>a</sup> WITH OXIDATION OF CELLULOSE AVOIDED

	Stock Bleached in Usual Way	Stock Bleached to Avoid Oxidation of Cellulose
α-Cellulose content, %:		
Before bleaching	94.8	94.8
After bleaching	93.4	94.6
Copper No.	2.26	1.36
Soly. in 3% NaOH soln., %	9.2	2.9
Color of 3% NaOH ext.:		
Hot	50	20
Cold	60	10
Cuprammonium viscosity	5.5	12.3
Color of bleached pulp	106	106
Color of bleached pulp after heating at 212° F. for 24 hr.	96	101

<sup>a</sup> A thoroughly cooked raw sulfite stock was digested with alkali to increase the α-cellulose content.

### Physical Condition of Pulp

The form in which cellulose is nitrated plays an important part in the results obtained (21, 28, 29, 38). When fibers are steeped in a bath consisting essentially of nitric acid, sulfuric acid, and water, esterification, oxidation, and hydrolysis may take place to a greater or lesser extent, according to the composition of the bath, the temperature, the ratio of liquid to cellulose, the intensity of agitation, and the physical condition of the cellulose. As nitration proceeds, water and heat are generated and nitric acid is consumed. If the reaction proceeds too rapidly, the acid immediately adjacent to the fiber or within it may grow so rich in water and so poor in nitric acid that hydrolysis is promoted. In addition, localized generation of heat may lead to oxidation and to hydrolysis of the cellulose. The extent to which agitation can be relied upon to moderate inequalities in acid composition and in temperature is limited by the bulkiness and the felting qualities of the fiber, and by the rate at which the reaction is proceeding. Too vigorous agitation may result in the disintegration of the fibers and in the conversion of the cellulose reaction products into nonrecoverable, finely dispersed material. If the temperature of the acid is lowered or the physical condition of the fiber is altered to retard the reaction, undesirable side reactions are much less likely to occur, but great care must be taken that all the cellulose

has reacted sufficiently before the batch is discharged from the nitrating pots, otherwise cloudiness may appear in the final nitrocellulose products and the yields may be low. If the cellulose is inadequately absorbent, the fibers may tend to float on the nitrating acid and may, through the excessive retention of the generated heat, cause "pot fires"—i. e., thermal decomposition of the contents of the nitrating vessel with attendant evolution of dense clouds of choking, corrosive, nitrous fumes.

Commercial nitration in this country is usually carried out in iron pots equipped with slow-speed agitators and having a capacity of about 30 to 35 pounds of fiber (cotton linters) and about 1500 to 1700 pounds of mixed acid. Approximately 25 to 35 minutes after the cellulose and the acid have been brought together in the pot, the charge is sluiced to a centrifuge which separates the bulk of the acid from the nitrated fiber. From the centrifuge the fibrous mat of cellulose nitrate is discharged into drowning basins where it is broken up by a generous stream of water, and the resulting pulplike suspension is flushed along through acid-proof pipe to the boiling—i. e., stabilizing—tanks, which are generally fitted with false perforated bottoms to permit draining and washing.

In this type of apparatus, wood pulp may be nitrated in at least three different forms: (a) as tissue or relatively thin paper, (b) in a shredded or fluffed linter-like condition, and (c) as chipped dryer sheets—that is, as clippings of the relatively thick sheets produced on the usual dryers with which all modern pulp mills are equipped.

### Nitration of Paper

Prior to about 1927 large quantities of rag and cotton paper were nitrated, notwithstanding the tremendous disparity in price between tissue and purified linters. Thus, in the early part of 1927 a first-grade tissue sold at 22 to 24 cents, a second-grade at 14 to 16 cents, and purified linters at 8 to 8.5 cents a pound. With tissue, however, more uniform results were being secured; clearer, cleaner, and smoother nitrate solutions were being realized, and a part of the difference in cost was balanced by the higher yields of nitrate obtained and the lower quantities of acid consumed.

Optimum papermaking conditions for purified wood pulp were established after the consideration of a multiplicity of factors. The paper must not be too thin, since the manufacture of tissue is expensive; shredded tissue is excessively bulky and hence tends to lessen the output of the nitrating apparatus and shreds of light-weight paper have a highly objectionable tendency to be blown about by air currents. If the paper is too thick, incomplete nitration is experienced within the customary time of nitration. In order that the retention of acid by the nitrated fiber in the centrifuge may not be excessive, the paper must be dense, but not too dense to permit reasonably rapid and smooth penetration by the nitrating acid. The density (i. e., compactness) of the paper can be controlled by the pressure applied to the wet press rolls through which the interfelted fibers pass on the way from the forming-wire of the paper machine to the dryers. It may also be influenced by the extent to which the fibers are "hydrated" in the beaters and in the Jordan engine, and by the severity of the calendering to which the dried paper may be subjected. Compacting at the wet end is to be preferred over calendering since the former operation makes for greater tonnage through the dryer. Hydration tends to toughen the paper, calendering to weaken it. Mechanical hydration of the cellulose may, however, lead under certain conditions to high residual acidity in the normally stabilized and washed nitrocellulose and hence must be carefully controlled; on the other hand, insufficient hydration may give rise to a lumpy or wild paper formation and to a strength inadequate to withstand the disintegrating action of the agitators in the nitrating pots and the severe

handling which the nitrocellulose undergoes during the centrifuging, drowning, stabilizing, washing, and dehydrating steps.

After many experiments, the optimum weight of paper was set at 30 pounds per 2880 square feet, the thickness at 0.043 inch, the Gurley test at 1 to 4 seconds for 100 cc. of air through an area 0.5 inch in diameter, the water crawl at 0.9 inch per minute in the machine direction and at 1.0 inch in the across direction. All pressing of the paper was done at the wet end of the papermaking machine. Stock chests, stock lines, felts, dryer clothing, etc., had to be maintained scrupulously clean; the water, including that circulated within the papermaking system ("white water") had to be free from all traces of size, and for best results the fresh water was treated to remove natural coloring matter.

A few of the more interesting and instructive of the numerous experiments made with purified wood pulp in paper form will now be described. Most of the work was done with acids leading to the lower nitrates—i. e., nitrocellulose containing 10.9 to 11.1 per cent nitrogen, and intended for conversion into celluloid—for it is more difficult to realize high yields and low acid retention values in the preparation of such nitrates.

### Effect of Varying Pressure on Undried Sheet

Waterleaf sheets of alkali-purified wood pulp are notably bulky, absorbent, and weak, especially if the stock is unhydrated when formed into paper—i. e., has not undergone a preliminary beating or working in water. In the preparation of the lower nitrates with the acid mixtures normally employed, such sheets may give low yields unless the temperature of nitration is so low that complete reaction requires a long time of contact with the acid. The poor yields may be due, however, not only to too rapid reaction, as previously explained, but to hydrolysis during drowning, possibly because of the large quantities of acid retained by the bulky sheets; they may also be due to insufficient bond between fibers, resulting in mechanical disintegration of the paper or of the fibers.

Results may be greatly improved if the thin sheet of inter-felted fibers is made more compact and tough by subjection to heavy pressure, as by passage through squeeze rolls, before it is dried. This is shown by the data in Table IV obtained with sheets of unbeaten purified wood pulp cut into 0.25-inch squares and nitrated to a nitrogen content of close to 11.0 per cent.

TABLE IV. EFFECT OF VARYING PRESSURE ON PAPER WEB BEFORE DRYING

Basis Weight of Paper Lb./2880 sq. ft.	Pressure Applied to Sheets before Drying Lb./sq. in.	Nitration Results			Appearance of Stabilizing Bath
		Yield %	Acid retention, per lb. nitrocellulose Lb.	Initial temp. rise ° F.	
30	100	127	3.8	3.8	Hazy
	500	132	3.1	4.3	Hazy
	1000	138	2.6	4.1	Hazy
	1500	145	2.1	4.0	Clear
	2000	149	1.5	3.1	Clear
60	100	128	3.4	4.0	Hazy
	500	141	2.0	3.1	Clear
	1000	143	1.8	2.9	Clear
	1500	130	3.0	3.6	Hazy
	2000	110	2.3	1.3	Hazy

With the highly pressed heavier sheets, the normal time of nitration (30 minutes) was too short for complete nitration; with the 30-pound sheets, however, complete nitration was secured in all instances.

The consolidating pressure ordinarily realized on the paper machine corresponds roughly to about 100–500 pounds per square inch as judged from the percentage moisture retained by the pressed stock, from the shrinkage in area of the sheets when air-dried without tension, and from the results of nitration.

### Effect of Beating upon Acidity of Stabilized Nitrocellulose

If the pulp is hydrated prior to formation into paper, it yields, with a given setting of the press rolls at the wet end of the papermaking machine, denser, less absorbent, and tougher sheets which tend to give higher yields of nitrocellulose and less retention of acid in the centrifuge than when the pulp is unhydrated.

From the data in Table V, the interesting fact is evident that the acidity of the finished nitrocellulose prepared according to these experiments is a function of the degree to which the pulp has been beaten. The samples listed in Table V were nitrated according to the normal procedure except that the mixed acid contained 19.0 per cent water, 22.0 per cent nitric acid, and 59.0 per cent sulfuric acid. Stabilization was effected by means of a 3-hour boil in water to which a few drops of the nitrating acid had been added to impart an acidity corresponding to about 0.5 per cent sulfuric acid. After the boil, the fiber was subjected to six treatments at room temperature with distilled water containing 25 p. p. m.

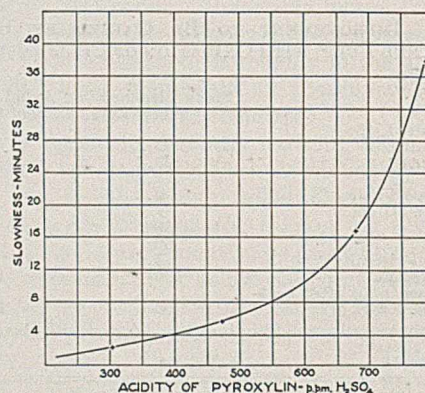


FIGURE 1. RELATION BETWEEN SLOWNESS OF PURIFIED WOOD PULP AND ACIDITY OF PYROXYLIN MADE IN THE LABORATORY FROM PAPER

sodium carbonate; each treatment involved the dilution of the stock from a concentration of 20–25 per cent nitrocellulose to 10–12 per cent, followed by its draining and squeezing in a nainsook bag to a concentration of 20–25 per cent. The samples were then air-dried for 16 hours at 30–35° C., and were finally tested. Figure 1 gives the observed relation between the acidity of the stabilized nitrate and the slowness or degree of hydration of the pulp.

In reviewing the data in Table V, obtained with nitrating papers of purified wood pulps beaten or hydrated to different degrees, one should bear in mind that the stabilizing boil was relatively short and mild in order that differences in the readiness or ease of stabilization of the numerous laboratory-prepared nitrocelluloses might be speedily and conveniently observed. As a consequence, the stabilities attained were lower than are normally realized in commercial practice—namely, a German test of at least about 20 minutes.

Although the stability varied, as might be expected, inversely as the residual acidity, certain samples of commercial nitrocellulose prepared from purified wood fiber showed the same German test as did samples of commercial nitro cotton

TABLE V. BEATING EXPERIMENTS IN PREPARATION OF NITRATING PAPER

Material nitrated	Purified wood pulp		Purified wood pulp				Purified wood pulp				Purified wood pulp	Domestic rag nitrating tissue	European cotton nitrating tissue	Cotton linters, nitrating grade
	Full load	Full load	Full load	Half load	Light load	One press skipped	Full load	Half load	Light load	One press skipped				
Time of beating, hr.	0.25	1.5	3.5				3				7	....	....	....
Slowness at head box, min.	2.33	2.11	5.58				38.2				17.3	....	....	....
Load on wet-end presses	Full load	Full load	Full load	Half load	Light load	One press skipped	Full load	Half load	Light load	One press skipped	Full load	....	....	....
Basis weight of paper (24 × 36 in., 480 sheets), lb.	27.4	31.1	29.2	31.0	32.9	33.7	32.0	29.4	31.3	33.0	31.5	36.4	11.2	....
Thickness, mils	4.3	4.0	4.3	4.4	5.5	5.9	3.5	3.6	4.2	5.0	3.8	5.2	2.7	....
Compactness	64	78	68	70	60	57	91	82	75	66	83	70	41	....
Air resistance, Gurley, sec.	4.5	3	4	3	2	1	20	19	7	4	18	13	4	....
Absorbency (water), in.:														
Along machine direction	1.60	1.95	1.68	1.68	2.10	2.50	0.83	0.85	1.23	1.60	0.90	1.00	1.80	....
Across machine direction	1.50	1.75	1.45	1.38	1.80	2.20	0.80	0.80	1.05	1.30	0.83	1.00	1.50	....
Nitrating yield, %	151	150	151	150	151	150	149	148	151	150	151	152	148	145
Color of nitrocellulose soln.	18	20	....	....	....	....	....	....	....	....	20	24	35	32
Acid retention, lb./lb. nitrocellulose	1.45	1.70	1.58	1.58	1.58	1.58	....	1.26	1.43	1.67	1.31	1.50	2.30	2.30
Initial temp. rise, ° F.	3.2	2.9	3.1	3.2	3.6	3.6	2.7	2.7	3.2	3.1	2.7	4.5	4.7	....
Nitrogen content, %	....	....	....	....	....	....	....	....	....	....	10.80	....	....	10.85
135° C. (275° F.) stability test, min.	18	16.5	12	11	11	11	11	10	10	10	10	17.5	11	12
Acidity, p. p. m. H <sub>2</sub> SO <sub>4</sub>	322	346	478	653	673	673	790	742	692	722	683	380	785	643

of about the same nitrogen content, despite the fact that the residual acidity was much higher for the nitrated wood pulps:

	Purified Wood Pulp Paper <sup>a</sup>	Cotton Linters <sup>a</sup>
Color of nitrated cellulose	20	22
Viscosity (12.2% soln.), sec.	46.7	77.1
Stability, min.	22	22
Nitrogen content, %	10.86	10.81
Acidity, p. p. m. H <sub>2</sub> SO <sub>4</sub>	1092	638

<sup>a</sup> Average of six commercial samples.

It would be interesting to determine whether the high residual acidity of the nitrocellulose prepared from highly beaten pulps was due merely to the more dense structure of the paper or to other, more obscure, factors.

**Mercerization of Wood Pulp Tissue**

The purity of the cellulose, the nitrating yield, the acid retention, and the clarity of solutions of the nitrate are all favorably affected if the nitrating paper is mercerized prior to nitration (62). Mercerization is attended by a reduction in pentosan content of the fiber and in the percentage of substances soluble in boiling dilute caustic soda solution; it also lessens the amount of coloring matter associated with the fiber, especially if an oxidant, such as sodium hypochlorite, is present in the mercerizing solution (61). The paper is rendered harder and denser by mercerization, in consequence of which it retains less spent acid upon centrifuging. Since the paper, particularly if of high alpha-cellulose content to begin with, needs to be mercerized only a few seconds, it is entirely feasible to treat it continuously and in sheet form. No trouble was experienced in running a 20-pound basis weight sheet through a bath of mercerizing solution 10 feet long at the rate of about 100 to 120 feet per minute, then between rubber squeeze rolls, thence into a shallow pan of hot water flowing countercurrent to the sheet, again between

squeeze rolls, thence through pans of cold wash water, again between squeeze rolls, and finally over a dryer. However, the waterleaf sheet remains intact only when the water in the pans next to the mercerizing bath is maintained at a temperature of above, say, 50° C. At lower temperatures the sheet softens decidedly in the water and may disintegrate with disconcerting readiness. If the tension on the sheet in the dryer is low, the mercerized paper crinkles so that, when cut and nitrated in the usual way, the cuttings show practically none of the bothersome tendency, characteristic of flat paper, to stick together in the nitrating acid.

The change in dimensions assumed by a light-weight sheet of purified wood fiber upon mercerization, washing, and air-drying with shrinkage freely permitted is indicated in Table VII. It is interesting to note that, of the total shrinkage in area, about half took place in the mercerizing bath and the rest during drying.

Another item of importance is the marked reduction in viscosity of nitrated cellulose brought about through mercerization of the tissue. The effect of preliminary mercerization upon the viscosity of nitrated cotton has been commented upon by Piest (37).

TABLE VI. RESULTS OF MERCERIZING A RELATIVELY IMPURE NITRATING PAPER MADE FROM PARTIALLY PURIFIED WOOD PULP

	Control			Mercerized Sheet		
Basis weight (24 × 36 in., 480 sheets), lb.	20			25		
α-Cellulose, %	92.2			94.1		
Soly. in 7.14% NaOH soln., %	15.0			6.9		
Color of 7.14% NaOH extract	150			70		
Pentosans, %	2.76			1.75		
Copper No.	2.92			2.20		
Temp. of nitration, ° F.	86	104	122	86	104	122
Time of nitration, min.	30	30	30	30	30	30
Nitrating yield, %	155	152	146	157	156	152
Acid retention, lb./lb. nitrocellulose	1.5	1.3	1.6	1.0	1.1	1.2
Color of nitrocellulose soln.	65	61	55	51	45	41
Viscosity, sec.	250 ±	43	11	65	20	7
Breaking length of film, yd.	6000	5800	5400	5700	6100	5500

<sup>a</sup> Composition of nitrating acid: 18.7 per cent water, 20.5 nitric acid, 60.8 sulfuric acid.

TABLE VII. CHANGES IN DIMENSIONS OF PAPER WHEN MERCERIZED

	Dimensions			% Shrinkage from Original			% Shrinkage from Step to Step		
	Machine direction	Cross direction	Area	Machine direction	Cross direction	Area	Machine direction	Cross direction	Area
	In.	In.	Sq. in.						
1. Original tissue, untreated	5.91	7.09	41.9	..	..	..	..	..	..
2. Tissue steeped 15 sec. in 18% NaOH soln. at 68° F.	5.55	6.40	35.5	6.1	9.7	15.3	6.1	9.7	15.3
3. Caustic-dipped sheets washed 30 sec. in boiling water	5.45	6.34	34.5	7.8	10.6	17.7	1.8	0.9	2.7
4. Same as 3, then treated with 20% acetic acid soln.	5.45	6.34	34.5	7.8	10.6	17.7	0	0	0
5. Same as 4, then washed in cold water	5.47	6.33	34.6	7.5	10.7	17.4	-0.4	-0.2	-0.3
6. Same as 5, then dried	5.05	6.04	30.5	14.5	14.8	27.2	7.7	4.6	11.9

### Parchmentization of Nitrating Paper (25)

Ordinarily, the added cost of mercerizing paper prepared from desinified purified wood pulp is hardly justified in commercial practice. The same appears to be true for parchmentization. Since the results obtained in experiments on parchmentization conducted in 1927 were highly interesting, they are given in Table VIII. Nitrating paper was steeped for 10 seconds in 72 per cent sulfuric acid solution at 15° C. (59° F.), then immersed in running cold water until free from acid, as judged by spotting the paper with methyl orange indicator. The paper thus parchmentized was dried and nitrated in the usual way. The experiment was repeated with parchmentizing solutions containing 1 and 5 per cent formaldehyde based on the weight of the sulfuric acid solution to retard the rate and hence to facilitate the control of parchmentization.

The extraordinarily low acid retention values obtained with parchmentized paper and the profound effect upon nitrocellulose quality when formaldehyde is present in the parchmentizing bath are noteworthy.

#### Effect of Fuzzy Edges

That the yield and the acid retention are influenced by the density and firmness of the purified wood pulp paper has been clearly demonstrated in the experiments described. Under the usual conditions of nitration, particularly in the preparation of the lower nitrates, the yield may be more sensitive to the

physical condition of the paper than might be imagined. Several years ago, tabs of nitrating paper,  $\frac{1}{8} \times 1$  inch in size, failed to give the expected high yield of nitrate during a laboratory demonstration at one of the large nitrating plants. A careful check revealed the fact that the slitters on the paper-cutting machine were dull and had imparted to the paper tabs slightly fuzzy edges in contrast with the sharp, clean edges obtained in the earlier laboratory experiments with hand-cut material. After the slitters had been properly adjusted, the following marked improvement in the results of nitration was noted:

	Edges Slightly Fuzzy	Edges Clean-Cut
Yield, %	147-147	152-150
Acid retention, lb./lb. nitro-cellulose	1.84-1.57	1.51-1.46

The difference in results would probably have been even greater if, rather than having been nitrated in glass beakers, the tabs had been nitrated on a commercial scale in the usual nitrating pots where the agitators would undoubtedly have caused additional disintegration at the edges of the tabs.

#### Work with Traces of Wax

The improvements gained by maintaining the paper in a firm, rather dense condition are to be attributed only partly to the greater mechanical strength thereby realized. Part or all of the gain can be ascribed to the retardation of the nitrating reaction, a conclusion which is borne

TABLE VIII. PARCHMENTIZATION OF A NITRATING PAPER MADE FROM PURIFIED WOOD PULP

Treatment	None	10 sec. in 72% H <sub>2</sub> SO <sub>4</sub> Soln. at 59° F.	10 sec. in 72% H <sub>2</sub> SO <sub>4</sub> soln. containing 1% formaldehyde at 59° F.	10 sec. in 72% H <sub>2</sub> SO <sub>4</sub> soln. containing 5% formaldehyde at 59° F.
Shrinkage in area, %	...	36	26	13
Copper No.	2.0	3.2	3.8	3.0
Soly. in 7.14% NaOH soln., %	8.2	19.6	19.7	13.5
Nitration Results				
Initial temp. rise, ° F.	4.3	0.7	2.2	3.8
Nitrating yield, %	153	142	155	152
Acid retention, lb./lb. nitrocellulose	1.5	0.67	0.93	0.95
Viscosity, sec.	52	23	135	170
Breaking length of film, yd.	5700	5900	6000	6100

TABLE IX. APPLICATION OF TRACES OF WAX TO NITRATING PAPER<sup>a</sup>

Treatment	Nitrogen Content, %	Nitrating Yield, %	% of Theoretical Yield
Control (av. of 6 nitrations)	11.16	152.0	97.4
Sheet dipped in water (av. of 9 nitrations)	11.18	154.0	98.7
Sheet dipped in emulsion of 1 part wax in 2000 parts water (av. of 2 nitrations)	...	154.2 <sup>b</sup>	...
Sheet dipped in 1 part wax in 4000 parts water (av. of 2 nitrations)	...	154.8 <sup>b</sup>	...
Sheet dipped in 1 part wax in 8000 parts water (av. of 2 nitrations)	11.19	154.8	99.2
Sheet dipped in 1 part wax in 11,000 parts water (av. of 3 nitrations)	11.17	155.1	99.5
Sheet dipped in 1 part wax in 20,000 parts water (1 nitration)	11.17	155.0	99.3

<sup>a</sup> Sheet dipped in water or wax emulsion, then redried, and nitrated.  
<sup>b</sup> Nitration slightly incomplete.

TABLE X. EFFECT OF PASSING 30-POUND NITRATING PAPER OVER A REVOLVING CYLINDER, PARTLY IMMERSSED IN A BATH AND DRYING

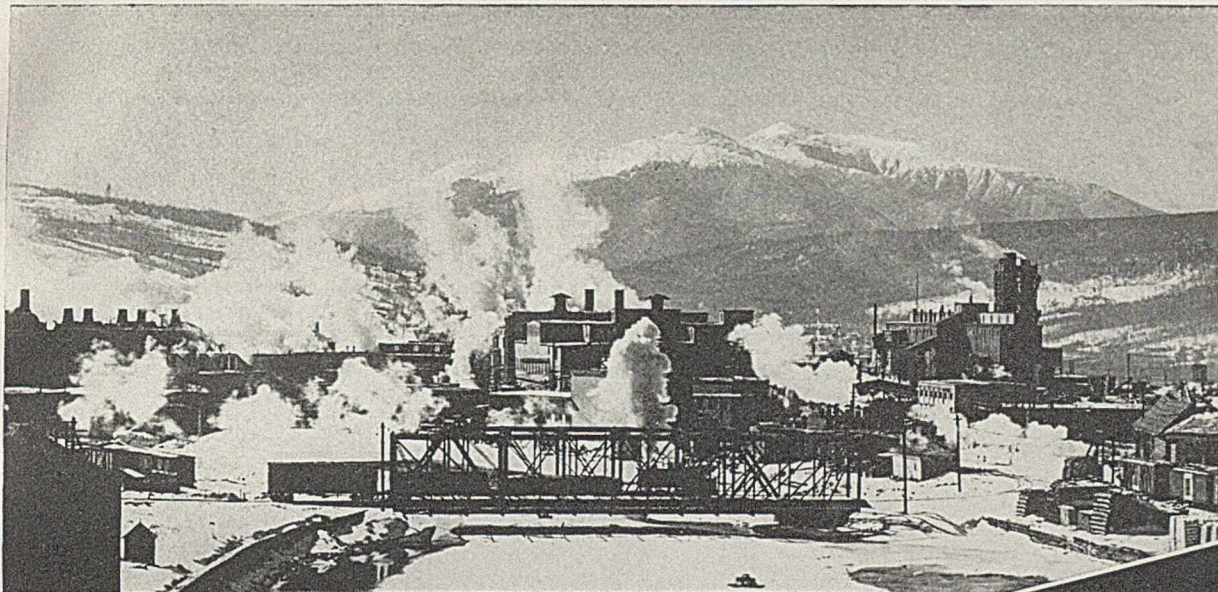
Treatment	Initial Temp. Rise, ° F.	Nitrogen Content, %	Nitrating Yield, %	% of Theoretical Yield	Acid Retention, Lb./Lb. Nitrocellulose	Color of Nitrocellulose Soln.
Control	3.1	11.09	150.8	97.0	1.36	18
Check control	2.7	11.10	151.0	97.0	1.26	18
Sheet passed over applicator roll partly immersed in water	2.7	11.14	153.3	98.3	1.31	18
Sheet moistened on one side by contact with roll partly immersed in emulsion of 1 part paraffin wax in 6000 parts water	2.5	11.13	154.7	99.3	1.29	18
Sheet moistened on both sides with 1 part wax in 6000 parts water	2.7	11.08	155.2	100.0	1.28	18
Sheet moistened on one side with 1 part wax in 12,000 parts water	2.3	11.10	154.7	99.5	1.29	18
Sheet moistened on both sides with 1 part wax in 12,000 parts water	2.5	11.10	155.7	100.0	1.42	18

TABLE XI. COMPARATIVE RESULTS OF NITRATING UNWAXED AND WAXED PAPER<sup>a</sup> WITH COTTON LINTERS

Sample	Paper (Control)	Waxed Paper	Linters	Paper (Control)	Waxed Paper	Linters	Paper (Control)	Waxed Paper	Linters
Quantity wax added, %	...	0.06	...	...	0.06	...	...	0.06	...
Temp. of nitration, ° F.	104	104	104	113	113	113	122	122	122
Initial temp. rise, ° F.	2.9	2.7	2.5	2.9	2.5	4.0	2.9	2.5	3.8
Nitrogen content, %	11.34	11.30	11.06	11.35	11.49	11.16	11.49	11.50	11.18
Nitrating yield, %	153.5	157.0	153.7	150.0	156.7	152.5	144.2	151.7	151.0
% of theoretical yield	97.7	100.0	99.2	95.3	98.8	97.8	91.9	95.6	96.7
Acid retention, lb./lb. nitrocellulose	1.18	1.18	1.22	1.23	...	1.28	1.31	1.18	1.26
Color of nitrocellulose soln.	18	18	36	18	18	36	18	18	36
Viscosity, sec.	35	63	5000	18	28	350	8	12	110
Breaking length of film, yd.	4900	5400	4300	5100	6200	4500	6300	5800	4400

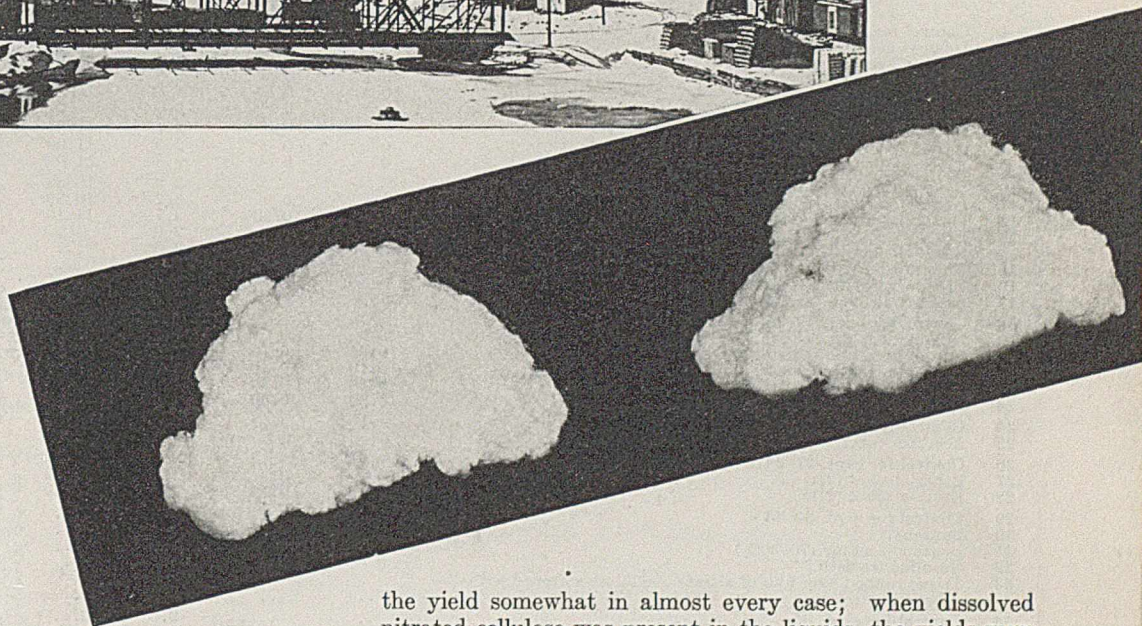
<sup>a</sup> Regular nitrating paper prepared from purified wood pulp nitrated with and without being waxed on both sides with a cold flatiron previously rubbed with a mixture of 25% paraffin wax and 75% stearic acid.





(Above) BROWN COMPANY MILLS, BERLIN, N. H.

(Right) SHREDDED MERCERIZED PURIFIED WOOD FIBER AND COTTON LINTERS



out by the results secured from the application to the nitrating paper of very small quantities of acid-repellent wax, for example, paraffin or paraffin mixed with stearic acid, prior to nitration (55, 60).

Although the amount of wax thus applied is altogether too low to affect the strength of the paper measurably, its influence upon the yield, and, incidentally, upon the clarity and brilliance of solutions of the nitrocellulose, is remarkable.

The nitrating yields are increased not only when very small quantities of wax are applied to the tissue, but also when the tissue is dipped in plain water and redried. This extraordinary fact is shown in Tables LX, X, and XI. This phenomenon may be due to the fact that minute traces of acid-repellent materials residing in the purified wood pulp are brought to the surface of the tissue when the water-dipped paper is redried, modifying the course of the nitration reaction in much the same way that traces of extraneously applied wax do.

#### Treatment of Tissue with Organic Liquids and Dilute Nitrocellulose

In order to check the hypothesis that water brings traces of acid-repellent material to the surface of the tissue, samples of nitrating paper were dipped in various organic liquids for 0.5 to 1 minute at room temperature and were nitrated after the liquids had been thoroughly removed by exposure to a stream of hot air (63). As a further check on this hypothesis, small quantities of nitrated cellulose were dissolved in some of the liquids prior to their application to the paper so as to leave a trace of the nitrate on the cellulosic raw material (43, 56). The data given in Tables XII and XIII show that preliminary treatment of the paper with the liquids increased

the yield somewhat in almost every case; when dissolved nitrated cellulose was present in the liquids, the yields were still further increased. Whether the tissue is predipped in water alone, in very dilute wax emulsion, in most of the organic liquid studied, or in the very dilute solutions of nitrocellulose, the rate at which it absorbs the nitrating acid is perceptibly diminished, but not necessarily to the point where excessive floating ensues. Nor does large-scale nitration of tissue treated with traces of wax indicate any tendency for the paper to fire in the pots or in the centrifuges.

#### Nitration of Shredded Pulp in Linter-like Form

In view of the expense involved in the conversion of pulp into paper, persistent efforts were made to develop a shredded, linter-like form of pulp which would give satisfactory nitration results. Early attempts gave disappointingly low yields and high acid retention values with regularity, especially in the preparation of the lower nitrates—i. e., nitrates containing about 11.0 per cent nitrogen. Although the results of nitration could in some instances be improved through treatment of the shredded stock with certain of the organic liquids listed in Table XIII, the results were too erratic to be considered satisfactory. It was noted, however, that occasionally the nitration of a sample of untreated shredded pulp gave better than average results. A search for the cause of this irregularity finally led to the discovery that the results depend upon the control of the moisture in the stock during shredding (57). This is shown in Figures 2 and 3, where the data of Tables XIV, XV, and XVI are plot-

TABLE XII. EFFECT OF VARYING TEMPERATURE OF NITRATION. NITRATING PAPER TREATED WITH ORGANIC LIQUIDS AND WITH DILUTE SOLUTIONS OF CELLULOSE NITRATE

Sample <sup>a</sup>	Nitration Temp., 104° F.			Nitration Temp., 113° F.			Nitration Temp., 122° F.			Nitration Temp., 131° F.		
	A	B	C	A	B	C	A	B	C	A	B	C
Initial temp. rise, ° F.	2.5	2.7	2.5	2.5	2.2	...	2.2	1.8	2.3	2.0	2.0	2.0
Nitrogen content, %	11.09	11.07	11.19	11.13	11.31	11.24	11.25	11.30	11.35	11.44	...	11.41
Yield, %	150.7	153.3	155.2	146.8	149.2	150.0	136.5	141.2	147.2	125.5	134.3	134.2
% of theoretical yield	96.8	98.8	99.5	95.2	95.0	95.8	87.4	90.0	93.5	79.3	...	85.1
Acid retention, lb./lb. nitrocellulose	1.1	1.0	1.2	1.9	1.2	1.4	1.2	1.2	1.3	1.6	...	1.5
Color of nitrocellulose soln.	18	18	18	18	18	18	18	18	18	18	18	18
Viscosity, sec.	50	58	80	15	22	27	12	11	14	5	5	6
Breaking length of film, yd.	4500	4800	5300	4700	3700	4900	4800	5000	4900	3800	4200	4600

<sup>a</sup> All samples nitrated for 30 minutes. A, control; B, paper dipped in isoamyl alcohol and redried; C, paper dipped in isoamyl alcohol containing 0.1% nitrated cellulose and redried.

TABLE XIII. TREATMENT<sup>a</sup> OF NITRATING PAPER WITH ORGANIC LIQUIDS AND WITH DILUTE SOLUTIONS OF NITROCELLULOSE

Expt. No.	Dipping Medium	Nitro-cellulose in Dipping Soln., %	Nitro-cellulose Retained by Sheet, %	Initial Temp. Rise, ° F.	Nitrogen Content, %	Nitrating Yield, %	% of Theoretical Yield	Acid Retention, Lb./Lb. Nitrocellulose
1	Control for expt. 2-6	0	0	2.9	10.98	152.0	98.3	1.6
2	Isoamyl acetate, tech.	0	0	1.8	11.10	154.3	99.2	1.2
3	Isoamyl acetate, tech.	0.3	0.60	1.8	11.25	156.3	99.7	1.4
4	Ether-alcohol (2:1)	0	0	2.0	11.03	152.7	98.6	1.3
5	Ether-alcohol (2:1)	0.3	0.85	1.8	11.20	152.8	97.8	1.2
6	Amyl-alcohol	0	0	2.0	...	153.8	...	1.2
7	Control for expt. 8-9	0	0	2.7	11.04	150.7	97.3	1.2
8	Gasoline	0	0	2.2	11.08	154.8	99.5	1.1
9	Kerosene	0	0	2.3	11.09	153.7	98.8	1.1
10	Control for expt. 11-17	0	0	2.9	10.89	149.3	97.0	1.2
11	Isoamyl acetate, redistd.	0	0	3.2	10.90	152.8	99.2	1.1
12	Isoamyl acetate, redistd.	0.3	0.60	2.7	11.10	154.0	99.0	1.1
13	Ether	0	0	2.0	...	153.3	...	1.2
14	Ethyl alcohol (98%)	0	0	2.5	...	154.0	...	1.2
15	Chloroform, redistd.	0	0	2.0	...	153.7	...	1.2
16	Trichloroethylene, redistd.	0	0	2.3	...	154.0	...	1.2
17	Isoamyl alcohol, tech. (pyridene-free)	0	0	1.8	...	154.2	...	1.2
18	Control for expt. 19-23	0	0	2.5	11.00	150.5	97.3	1.2
19	Isoamyl acetate, redistd.	0	0	2.5	11.04	154.3	99.5	1.2
20	Isoamyl acetate, redistd.	0.05	0.10	2.5	11.20	155.3	99.5	1.2
21	Isoamyl acetate, redistd.	0.10	0.20	2.5	11.23	155.7	99.5	1.2
22	Isoamyl acetate, redistd.	0.20	0.40	2.3	11.21	155.2	99.3	1.2
23	Isoamyl acetate, redistd.	0.30	0.60	2.5	11.30	155.5	99.0	1.2
24	Control for expt. 25	0	0	2.3	11.06	151.7	97.7	1.1
25	Acetone + 0.1% isoamyl acetate, both redistd.	0	0	2.2	11.06	154.7	99.6	1.2
26	Control for expt. 27-28	0	0	2.3	11.10	147.0	94.5	1.2
27	Ether-alcohol (2:1)	0	0	2.5	11.09	153.0	98.3	1.1
28	Ether-alcohol (2:1)	0.05	0.10	2.0	11.20	154.5	98.8	1.0
29	Control for expt. 30-33	0	0	2.5	...	146.5	...	1.2
30	Benzene	0	0	2.2	...	152.5	...	1.2
31	Benzene-acetone (70-30%)	0	0	2.0	...	155.5	...	1.2
32	Gasoline (redistd.)	0	0	2.0	...	155.2	...	1.1
33	Tissue rubbed over film of nitrated cellulose softened with benzene-acetone	...	...	2.9	...	152.7	...	1.1
34	Control for expt. 35	0	0	2.5	...	143.8	...	1.2
35	Benzene	0	0	2.3	...	154.2	...	1.2
36	Control for expt. 37-39	0	0	2.3	...	145.0	...	1.3
37	Methyl alcohol, redistd.	0	0	2.2	...	147.8	...	1.3
38	Benzene-methyl alcohol (70-30%)	0	0	2.2	...	149.8	...	1.2
39	Benzene-methyl alcohol (70-30%)	0.10	0.20	2.2	...	152.7	...	1.2

<sup>a</sup> Tissue dipped in various liquids or solutions of nitrated cellulose 0.5 to 1 minute, air-dried, cut up into 0.25-inch squares, dried 1 hour at 212° to 218° F., and nitrated in the usual way at 104° F.

TABLE XIV. EFFECT OF SHREDDING SULFITE PULP AT DIFFERENT MOISTURE CONTENTS

Fiber content during shredding, %	31.0	42.6	49.7	53.8	60.5
Nitrating yield, %	117.5	133.2	136.5	135.0	128.2
Acid retention, lb./lb. nitrocellulose	3.1	2.9	2.7	3.1	3.0
Appearance of stabilizing bath	Hazy	Slightly hazy	Clear	Clear	Clear

TABLE XV. EFFECT OF SHREDDING PURIFIED WOOD PULP AT DIFFERENT MOISTURE CONTENTS

	Fiber Content during Shredding (Bone-Dry Basis), %	Nitration Results		Appearance of Stabilizing Bath
		Yield, %	Acid retention, lb./lb. nitro-cellulose	
Dryer stock moistened to	15.0	117.3	3.8	Very hazy
Slush stock squeezed to	23.6	125.8	2.4	Very hazy
Dryer stock moistened to	25.0	126.3	2.9	Very hazy
Dryer stock moistened to	35.0	137.7	2.4	Very hazy
Slushed stock air-dried at room temp. to	45.0	145.2	2.6	Very hazy
Slushed stock air-dried at room temp. to	45.1	144.2	2.6	Hazy
Slushed stock air-dried at 170° F. to	47.2	143.0	2.9	Hazy
Slushed stock air-dried at room temp. to	52.0	144.5	3.3	Clear
Slushed stock squeezed to	52.0	144.5	3.1	Clear
Slushed stock air-dried at room temp. to	53.0	139.3	2.8	Hazy
Slushed stock air-dried at room temp. to	55.3	138.3	3.2	Hazy
Slushed stock air-dried at 180° F. to	68.7	124.3	3.5	Hazy
Slushed stock air-dried at 180° F. to	74.0	120.5	3.7	Hazy
Slushed stock air-dried at room temp. to	81.0	105.2	4.3	Hazy
Slushed stock air-dried at room temp. to	90.0	94.2	4.2	Hazy

ted. If the stock is mercerized and then shredded in the presence of a controlled amount of moisture, the results are even further improved, equaling in most respects those obtainable with high-grade linters (44, 59).

Not only is the moisture content during shredding a dominating factor in the results of nitration, but the shreds must be as fine as possible for best results, as appears from Tables XVIII and XIX. However, if the pulp is mercerized prior to being shredded, it lends itself more readily to uniform shredding, and hence the shredding operation need not be so carefully supervised as in the case of unmercerized fiber. Mercerization, therefore, not only leads to improved nitrating qualities in the pulp (13A), but also to convenience in shredding; in addition (Figure 2), it widens the range of moisture content within which the stock must be shredded for optimum nitrating results.

TABLE XVI. EFFECT OF SHREDDING MERCERIZED PURIFIED WOOD PULP<sup>a</sup> AT DIFFERENT MOISTURE CONTENTS

Nitrated to About 11% Nitrogen Content <sup>b</sup>										
Fiber content during shredding, %	4.6	16.0	19.8	22.6	29.4	30.4	32.6	39.2	40.0	50.5
Nitrating yield, %	133.8	139.2	144.0	148.3	152.0	153.3	154.5	155.3	153.3	154.0
Acid retention, lb./lb. nitrocellulose	3.5	3.0	2.8	2.7	2.4	2.2	1.9	2.0	2.2	2.0
Nitrated to About 12% Nitrogen Content <sup>c</sup>										
Fiber content during shredding, %	16.6	21.8	33.8	41.0	50.0	61.4	76.4	86.0	95.0	
Nitrating yield, %	162.0	163.5	163.7	163.3	162.3	162.3	161.8	161.5	161.0	
Acid retention, lb./lb. nitrocellulose	1.5	1.5	1.4	1.4	1.4	1.4	1.4	1.4	1.5	1.6

<sup>a</sup> Purified wood pulp mercerized in 18 per cent NaOH solution at 68° F. for 15 minutes, then washed, dried to different moisture contents, finely shredded, bone-dried, and nitrated.  
<sup>b</sup> Composition of nitrating acid: 18.7% H<sub>2</sub>O, 20.5% HNO<sub>3</sub>, 60.8% H<sub>2</sub>SO<sub>4</sub>.  
<sup>c</sup> Composition of nitrating acid: 17.6% H<sub>2</sub>O, 21.7% HNO<sub>3</sub>, 60.7% H<sub>2</sub>SO<sub>4</sub>.

TABLE XVII. MERCERIZED PURIFIED WOOD PULP SHREDDED AT 50 PER CENT MOISTURE CONTENT, BONE-DRIED, AND NITRATED AT 104° F. TO DIFFERENT NITROGEN CONTENTS

Composition of acid:				
H <sub>2</sub> O, %	14.7	16.7	18.7	20.7
HNO <sub>3</sub> , %	21.5	21.0	20.5	20.0
H <sub>2</sub> SO <sub>4</sub> , %	63.8	62.3	60.8	59.3
Ratio HNO <sub>3</sub> to H <sub>2</sub> SO <sub>4</sub>	1:2.97	1:2.97	1:2.97	1:2.97
Nitration data:				
Nitrating yield, %	166.7	162.8	154.5	119.5
Acid retention, lb./lb. nitrocellulose	1.5	1.7	1.9	3.6
Nitrogen content, %	12.62	12.20	11.32	9.98
% of theoretical yield	99.2	99.0	98.4	81.0

TABLE XVIII. PURIFIED WOOD PULP SHREDDED WITH RAPIDLY ROTATING BLADES

Fiber Content during Shredding, Bone-Dry Basis, %	Time of Shredding, Min.	Nitration Results—		Appearance of Stabilizing Bath
		Yield, %	Acid retention, lb./lb. nitrocellulose	
28	0.75	124.5	3.5	Very hazy
	1.5	125.7	3.2	Hazy
	3	127.5	2.9	Slightly hazy
	4	128.0	2.8	Very hazy
39	0.75	137.3	3.2	Hazy
	1.5	137.7	3.2	Slightly hazy
	3	142.3	2.8	Slightly hazy
	4	144.5	2.8	Very hazy
47	0.75	138.5	3.3	Hazy
	1.5	143.5	3.1	Almost clear
	3	144.0	2.9	Clear
	4	147.5	3.0	Clear
51	0.25	143.8	3.0	Hazy
	0.75	148.5	2.9	Almost clear
	1.5	148.7	2.7	Clear
	3	148.7	2.5	Clear
65	0.75	141.2	3.3	Slightly hazy
	1.5	144.5	3.1	Almost clear
	3	144.7	3.1	Clear
	4	144.3	3.3	Clear

If the pulp is too wet during shredding—for example, about 80 per cent moisture content—it yields shreds which are comparatively hard and stringy when dried. As the moisture content during shredding is reduced, the dried shreds become bulkier and less stringy, until, with dry pulp as the starting material the final product is fluffy and shows a high content of dust or “fly” when worked between the fingers. With mercerized pulp, the changes in the physical nature of the shreds with variations in moisture content during shredding are of a similar order. However, a final product prepared by shredding such pulp with properly controlled moisture content resembles cotton linters much more closely in feel and in appearance than one prepared from unmercerized pulp under comparable conditions.

Experiments show that the same curves for nitrating yield and acid retention are obtained whether the pulp is dewatered to a given moisture content before being shredded or is completely dried and rewet to the given moisture content (Table XV). This is of commercial significance, for in the first case

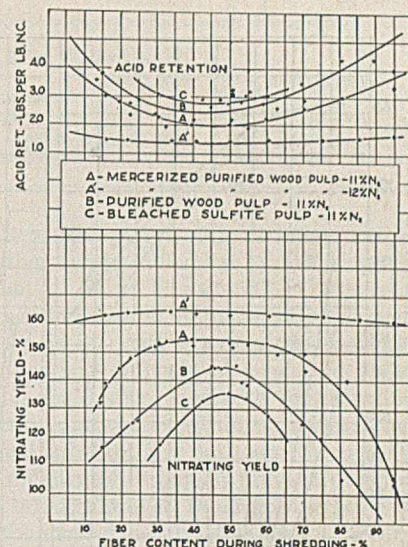


FIGURE 2. EFFECT OF VARYING THE MOISTURE CONTENT OF PULP DURING SHREDDING

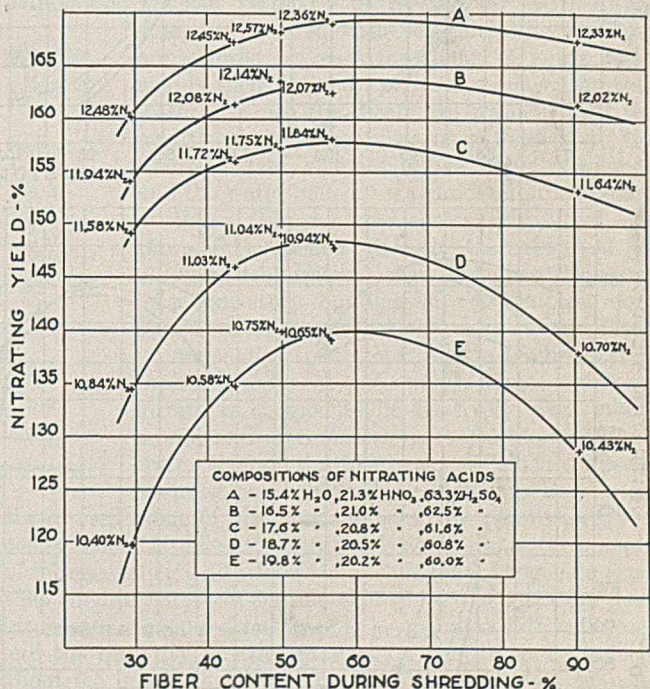


FIGURE 3. EFFECT ON NITRATING YIELD AND NITROGEN CONTENT OF SHREDDING PURIFIED WOOD PULP AT DIFFERENT MOISTURE CONTENTS

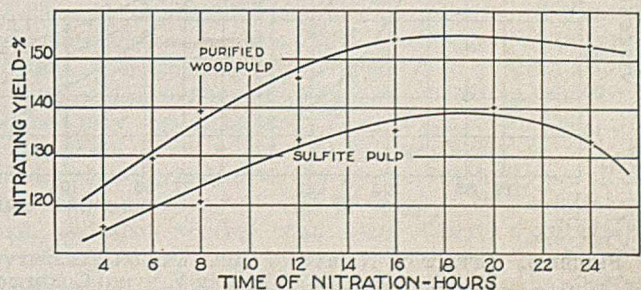


FIGURE 4. NITRATION OF PURIFIED WOOD PULP AND OF SULFITE PULP IN DRYER-BOARD FORM AT 59° F. FOR DIFFERENT PERIODS (Composition of mixed acid, 18.7 per cent water, 20.5 per cent nitric acid, 60.8 per cent sulfuric acid)

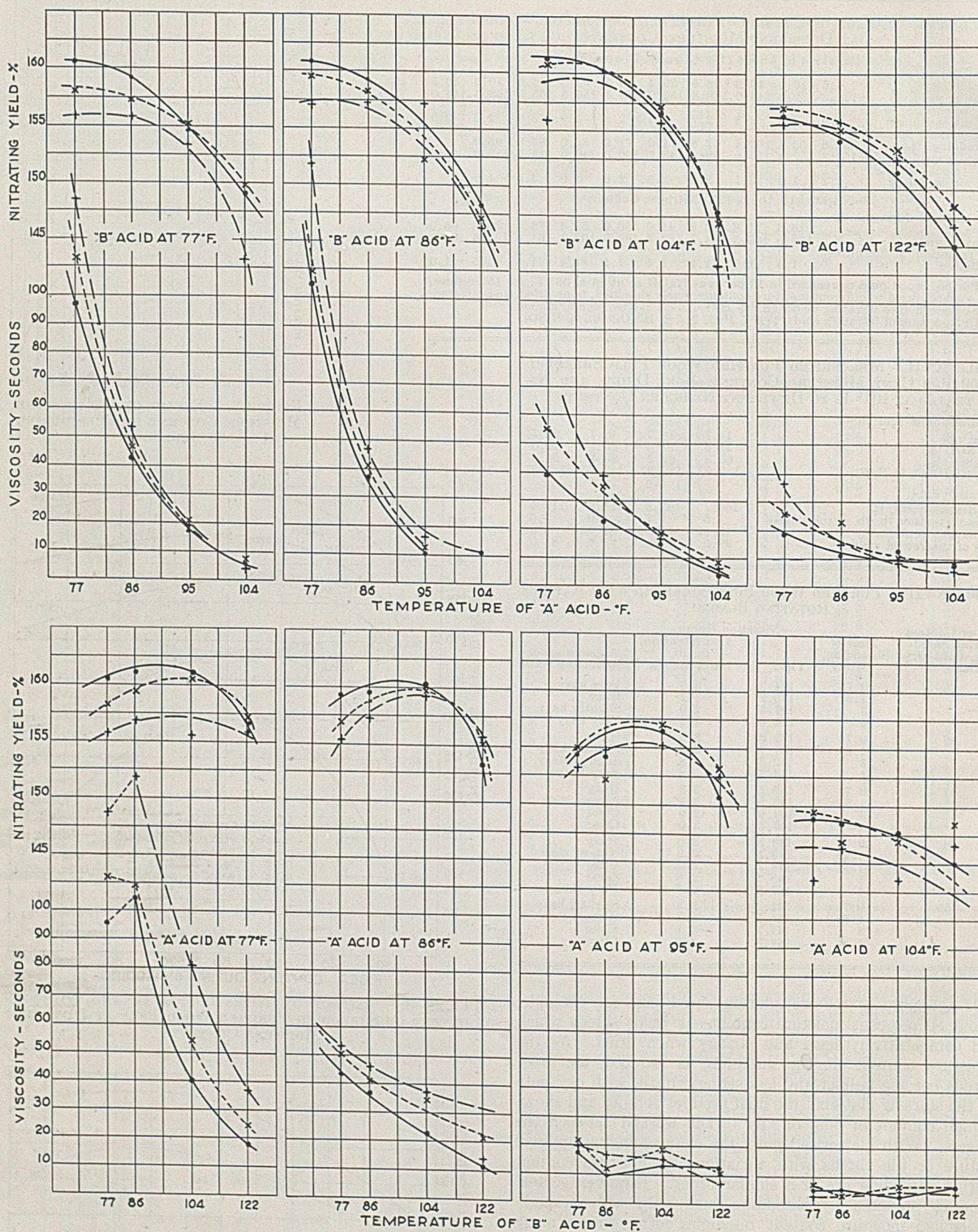


FIGURE 5. EFFECT ON NITRATING YIELD AND ON VISCOSITY OF NITRATING PURIFIED WOOD PULPBOARD BY TWO-ACID PROCESS UNDER VARYING CONDITIONS OF TEMPERATURE AND TIME

- + Nitrated 3 hours in A acid, 1 hour in B acid
- x Nitrated 3 hours in A acid, 2 hours in B acid
- Nitrated 3 hours in A acid, 3 hours in B acid
- A acid, 17.0 per cent water, 33.2 per cent nitric acid, 49.8 per cent sulfuric acid
- B acid, 18.7 per cent water, 20.5 per cent nitric acid, 60.8 per cent sulfuric acid

TABLE XIX. PURIFIED WOOD PULP SHREDDED WITH RAPIDLY ROTATING WIRE BRUSH

	Stock Once through Brush Shredder					Stock Twice through Brush Shredder					Stock Four Times through Brush Shredder				
	22.3	32.2	38.6	50.0	61.0	22.6	32.2	38.2	49.2	62.0	23.3	33.8	40.8	52.2	65.6
Fiber content during shredding, %	114.3	121.0	133.8	135.3	138.8	131.3	135.3	147.5	148.7	148.8	131.0	144.7	150.0	150.2	152.5
Nitrating yield, %	Hazy	Hazy	Clear	Clear	Clear	Hazy	Hazy	Hazy	Clear	Clear	Hazy	Hazy	Clear	Clear	Clear
Appearance stabilizing bath															

it permits the preparation of the desired quality of shreds economically at the pulp mill from slush stock and in the second case enables the realization at the nitrating mill of the same quality of shreds from pulpboard—i. e., the form in which pulp is most conveniently shipped and stored.

The nitration of purified wood fibers shredded under optimum conditions is at present being successfully practiced on a commercial scale. The pulp is supplied in the form of pulpboards which are moistened at the nitrating plant with the proper quantity of water, then coarsely shredded in the usual cotton picker, and finely shredded in a hammer mill. The shreds are dried in the cotton dryer with which nitrating plants are usually equipped and are nitrated and generally handled throughout the process like cotton linters. Since the shreds go into the cotton dryer much more moist than cotton linters, the capacity of the dryer may have to be increased if it is to keep pace with the nitrating equipment.

try, and a pioneer in nitrocellulose film and silk manufacture, ingeniously overcame this serious difficulty by lowering the temperature of nitration to 5–15° C. (41–59° F.), thereby retarding the rate of reaction so that diffusion of nitric acid from the main body of acid into the sphere of the reaction within the sheet structure and diffusion of generated water in the opposite direction could keep pace with the nitration reaction. The composition of the acid within the sheet structure was thus maintained substantially optimum throughout the reaction—that is, sufficiently strong to prevent destructive side reactions. In order, however, to ensure nitration of the innermost fibers of the sheet structure, it became necessary to extend the time of nitration to 12–20 hours (38). Planchon's process has been successfully practiced on a commercial scale near Rouen, France, during the past seven or eight years in the manufacture of a superior grade of celluloid. The pulpboards, stacked vertically in rectangular earthenware vats, are covered with cold nitrating acid and are allowed to react for about 24 hours. The acid is then drained away and replaced by cold water in which the sheets are washed until the acidity of the nitrate has been reduced to the desired extent, whereupon live steam is applied and the water boiled for a predetermined period of time. The nitrated sheets, still intact, are thoroughly washed and are then removed for pulping, dehydration, etc. The nitrating house is a one-story building of the simplest construction, no centrifuges are used, and the plant is unusually free from nitrous fumes. The capital investment per ton per day of stabilized nitrate is claimed to be relatively low; labor, power, and maintenance cost are likewise moderate. Among the drawbacks of Planchon's process must be mentioned the following: Because of

TABLE XX. COMPARISON OF WOOD PULP AND LINTERS IN VARIOUS FORMS

	Purified Wood Pulp, 30-Lb. Paper	Purified Wood Pulp, Shredded	Mercerized Purified Wood Pulp, Shredded	Double-Cooked Linters	Purified Linters
$\alpha$ -Cellulose, %	94.8	94.8	98.5	93.1	99.2
Cuprammonium viscosity	5.0	5.0	3.2	3.1	60.0
Resins, %	0.03	0.03	0.03	...	0.07
Ash, %	0.09	0.09	0.05	...	0.08
Form in which nitrated	0.25-in. squares of 30-lb. paper	Shredded at about 50% dryness	Shredded at about 50% dryness	Bulk	Bulk
Yield, %	151.7	150.0	155.7	156.8	157.0
Acid retention, lb./lb. nitrocellulose	1.2	2.3	2.0	1.9	2.0
Color of nitrocellulose soln.	18	22	18	36	19

### Nitration of Pulpboard

Because of the expense of drying the wet shreds, the cost of converting pulp into a properly shredded product ready for nitration may ordinarily be not much different from that of converting it into tabs of 30-pound paper. The cheapest form in which dry pulp is prepared, however, is so-called dryer stock or pulpboards—that is, boards of pulp about 0.030 to 0.040 inch thick, such as are usually supplied to paper-making and viscose rayon mills. The modern pulp dryer is a huge machine capable of forming into sheets and drying at relatively low cost 150 or more tons of pulp per day. Such sheets or boards, when used in the manufacture of rayon, are steeped in and soaked with sodium hydroxide liquor of mercerizing strength prior to shredding and xanthation. Because of the swelling and softening action of the caustic soda solution on the sheets, they are easily penetrated by the soaking liquor despite the fact that they maintain their integrity to a surprising degree. When nitrated, however, pulpboards are altogether too thick to be properly acted upon by the usual nitrating acids, for the surface of the sheets tends to gelatinize, and penetration of the acids into the boards is so slow that the mixed acid within the boards becomes improvised in nitric acid and enriched in water to the point where hydrolysis of the cellulose becomes excessive, with consequent impairment of yield and quality of the nitrated product. Planchon, long connected with the indus-

the limited range of nitrating temperatures permissible, viscosity control is difficult; nitration is nonuniform, the outside of the sheets being nitrated to a much higher nitrogen content than the interior; an enormous inventory of nitrating acid in process is required relative to the output of nitrocellulose; and the quantity of acid retained by the drained sheets is about 0.5 pound higher per pound of nitrocellulose than in the case of linters nitrated and centrifuged in the usual way.

Most of these disadvantages are overcome in a practical process of nitration developed by the Brown Company (51). The pulpboards, cut into pieces of convenient size, are nitrated at about 40° C. (104° F.) for about 1 to 3 hours with a mixed acid unusually rich in nitric acid and somewhat low in water content. Conveniently expressed, the ratio of nitric acid to sulfuric acid should be greater than one to two, and the water content may vary from about 12 to 25 per cent. The exact composition of the mixed acid depends upon the type of nitrocellulose desired, upon the time available for nitration, upon the ratio of mixed acid to cellulose in the nitrating bath, and upon whether small pieces of dryer board are to be nitrated and the spent acid recovered with the aid of a centrifuge, or whether relatively large sheets are to be nitrated in vats such as Planchon uses and the acid recovered by draining, etc.

Because of the comparative fluidity of the unusual acid mixture and its greatly reduced tendency to gelatinize the

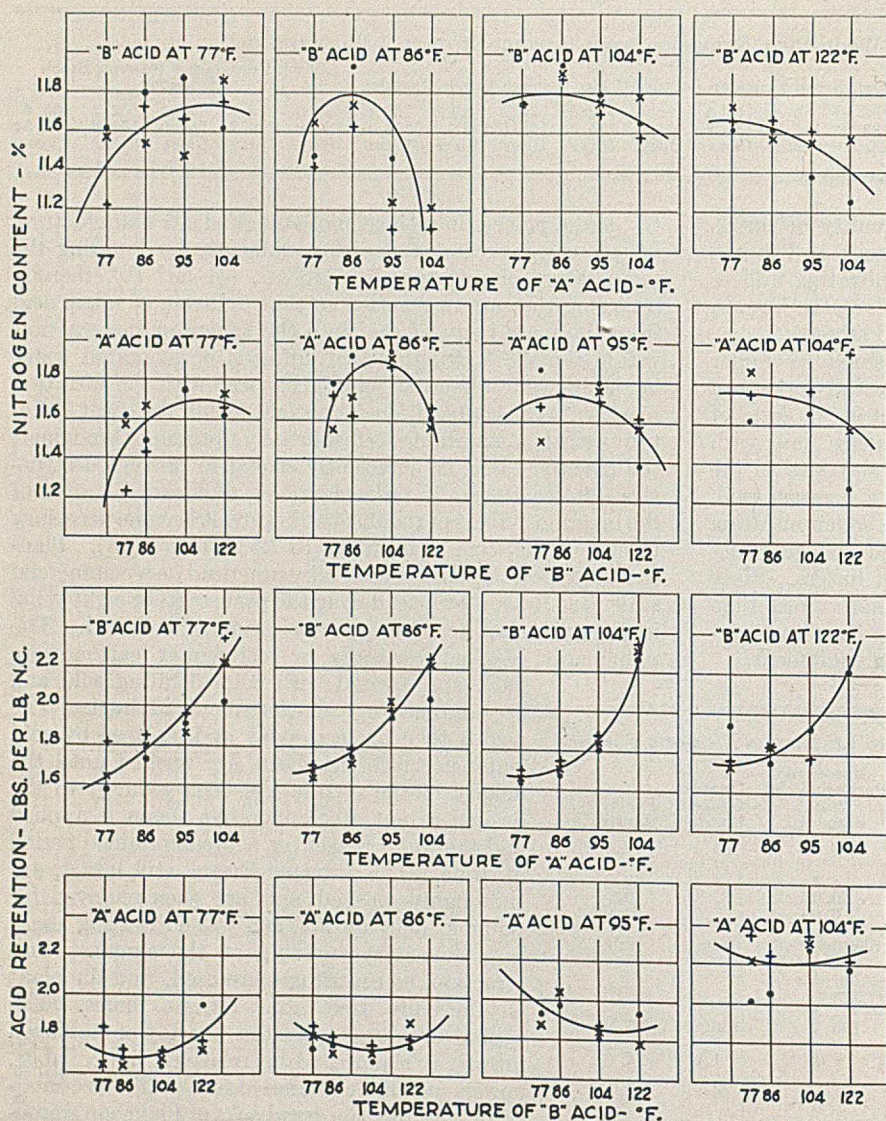


FIGURE 6. EFFECT ON NITROGEN CONTENT AND ON ACID RETENTION OF NITRATING PURIFIED WOOD PULP BY TWO-ACID PROCESS UNDER VARYING CONDITIONS OF TEMPERATURE AND TIME

- + Nitrated 3 hours in A acid, 1 hour in B acid  
 × Nitrated 3 hours in A acid, 2 hours in B acid  
 • Nitrated 3 hours in A acid, 3 hours in B acid  
 A acid, 17.0 per cent water, 33.2 per cent nitric acid, 49.8 per cent sulfuric acid  
 B acid, 18.7 per cent water, 20.5 per cent nitric acid, 60.8 per cent sulfuric acid

cellulose, penetration into the stock is fairly rapid. The high nitric acid content and the relatively low water content of the mixed acid cooperate to suppress hydrolysis of the cellulose even within the innermost portions of the sheets, yet the composition of the acid within the stock is always such as to give the desired properties in the nitrated cellulose.

and later in one of more nearly normal composition (50). Ordinarily the first acid is somewhat higher in water content than in the single-acid process, thereby causing the nitration to fall short of completion in the first stage. The reaction is completed when the partially nitrated fibers are finally treated with the second acid.

With sheets cut into small pieces, up to about three to six times the usual quantity of cellulose can be handled per batch in the ordinary nitrating pot and in the centrifuges, for the pulpboard is very dense as compared with cotton in bulk. The ratio of acid to cellulose during nitration is correspondingly lowered, and hence the output of a nitrating pot is much higher than with linters, tissue, or shredded pulp (36, 51).

The weight of acid retained in the centrifuges is low—about 1.0 to 1.5 pounds of spent acid per pound of nitrocellulose, depending upon the compactness of the dryer board. The lower figure is obtained when the compactness is about 90 and the upper when the compactness is 65, but the retained acid is rich in the more expensive nitric acid. Although the first cost of the nitrating acid is high and relatively large volumes of spent acid may have to be returned to the nitric acid plant for recovery, the high yields of nitrocellulose and the savings in cost of cellulosic raw material, labor, steam, etc., are more or less adequate compensation. In addition, the quality of the nitrocellulose obtained is outstandingly good, not only because of the inherent characteristics of the highly refined wood pulp used as raw material, but because of the favorable composition of the mixed acids. The process is eminently practical and is being conducted on a commercial scale in this country in the manufacture of nitrocellulose for plastics.

### Two-Stage Nitration

In order to facilitate the fortification of the unusually rich mixed acid used in the pulpboard process described, a two-stage method of nitration was devised where the cellulose is first steeped in an acid mixture abnormally rich in nitric acid content,

TABLE XXI. NITRATION<sup>a</sup> OF FIBERS IN PULPBOARD FORM AT 59° F. FOR VARIOUS PERIODS

Time, hr. Temp., ° F.	Bleached Sulfito Fiber <sup>b</sup>						Purified Wood Fiber <sup>c</sup>				
	4	8	12	16	20	24	6	8	12	16	24
Nitrating yield, %	116	120	133	135	140	133	59	59	59	59	59
Acid retention, lb./lb. nitrocellulose	...	3.1	3.6	4.3	3.5	4.8	...	...	...	2.1	2.7
Remarks	Incompletely nitrated; stabilizing bath clear	Almost completely nitrated; stabilizing bath hazy	Stabilizing bath hazy	Stabilizing bath clear	Stabilizing bath clear	Stabilizing bath clear	Incompletely nitrated	Incompletely nitrated	Nitration slightly incomplete	...	...

<sup>a</sup> Composition nitrating acid: 18.7% H<sub>2</sub>O, 20.5% HNO<sub>3</sub>, 60.8% H<sub>2</sub>SO<sub>4</sub>.

<sup>b</sup> Basis weight of dryer sheet, 280 pounds (24 × 36 inches, 480 sheets); thickness, 0.032 inch; compactness, 90.

<sup>c</sup> Basis weight of dryer sheet, 295 pounds; thickness, 0.037 inch; compactness, 80.

In one example of the practice of the two-stage process, the sheets are fluted and stacked in convenient units (Figure 7), so arranged as to prevent more than occasional line contact between neighboring sheets and to permit free access of acid to substantially all portions of the sheets being nitrated (52). The sheet units are bone-dried in an air oven and are transferred to rectangular chrome steel vats containing acid at 30° to 50° C. (86° to 122° F.). If a nitrogen content of, say, 11 per cent is desired in the final product, this acid may have the composition 17.0 per cent water, 33.0 per cent nitric acid, and 50.0 per cent sulfuric acid. If 12 per cent nitrogen is wanted, the composition is changed to 16.5 per cent water,

TABLE XXII. EFFECT OF VARYING COMPACTNESS OF PURIFIED WOOD PULPBOARD UPON NITRATING YIELD AND ACID RETENTION<sup>a</sup>

Basis weight (24 × 36 in., 480 sheets), lb.	254	248	236	258	265
Thickness, in.	0.056	0.048	0.041	0.041	0.034
Compactness	45	52	58	63	78
Nitrating yield, %	153.8	154.5	154.3	152.5	144.3
Acid retention, lb./lb. nitrocellulose	3.77	2.44	1.92	1.77	1.75
Nitrogen content, %	11.50	10.96	10.87	10.75	10.25
% of theoretical yield	96.8	100	100	100	96.8

<sup>a</sup> Acid compositions: A acid, 16.21% H<sub>2</sub>O, 33.82 HNO<sub>3</sub>, 49.97 H<sub>2</sub>SO<sub>4</sub>; B acid, 18.03% H<sub>2</sub>O, 21.10 HNO<sub>3</sub>, 60.87 H<sub>2</sub>SO<sub>4</sub>. Nitrating conditions, stock treated 2 hours in A acid at 86° F. followed by 2 hours in B acid at 104° F.

36.0 per cent nitric acid, and 47.5 per cent sulfuric acid. A ratio of about 50 pounds of acid per pound of cellulose is employed. After about 2 or 3 hours, depending upon the thickness and the density of the sheets, the acid is drained away and is replaced by one having the composition 18.7 per cent water, 20.5 per cent nitric acid, and 60.8 per cent sulfuric acid for 11 per cent nitrogen, and 17.8 per cent water, 21.2 per cent nitric acid, and 61.0 per cent sulfuric acid for 12 per cent nitrogen. Since the nitrogen content in the final product is dependent somewhat upon the quantity of the first acid retained by the sheets and thereby carried

over into the second acid, the compositions of the acids employed are correspondingly dependent upon the density and weight of the sheets.

Table XXII and Figure 8 show that with pulpboard commercially available, good combinations of yield and acid retention were realized with sheets 60 to 65 in compactness. In all probability, the greater the pains taken at the pulp mill to prepare the dryer sheets free from clumps of fiber—that is, the more uniform the “formation” of the sheets—the higher the

compactness permissible, with consequent lowering of the acid retention values. The optimum condition of nitration including composition of the acids, duration of nitration, size of apparatus, etc., compactness and weight of the pulpboard, obviously depend upon the relative costs of nitric acid, sulfuric acid, pulpboard, labor, quality of nitrocellulose desired, size of plant, cost of equipment, and other similar factors.

The acid retained by the sheets at the completion of nitration may be recovered to a material extent if the spent acid is displaced by water instead of being simply drained away. Sheet nitration lends itself surprisingly well to a displacement process (53) because of the fact that displacement can be effected at as high as the remarkably fast rate of 24 inches per hour without causing excessive mingling of water and acid with attendant overheating and resultant loss in yield and in acid. In this respect, the sheets behave quite differently than linters (Figure 9).

### Half-Second Nitrocellulose from Pretreated Cellulose

The modern lacquer industry owes much of its remarkable growth to the discovery in 1919–22 of practicable methods for greatly reducing the solution viscosity of nitrocellulose without excessive impairment of film strength or durability (9, 10). The lower the viscosity of the nitrocellulose, the more of it can be dissolved in solvent mixtures to give free-flowing lacquers, with corresponding savings in solvent cost and in labor of application. Most of the low-viscosity nitrocellulose is today being produced by the digestion of high-viscosity nitrocellulose at elevated temperature and pressure, a procedure suggested in 1899 by Schulz (48) for the stabilization of nitrocellulose rather than for the reduction of viscosity. Since the hazards of plant-scale digestion in the usual type of pressure vessel have led to several disastrous explosions, Milliken devised the relatively safe continuous-digesting system now being used by the Hercules Powder Company (27).

It has long been appreciated that pretreatment of the cellulosic raw material with acidic or oxidizing reagents leads to a reduction in the viscosity of the nitrate prepared in the usual way and stabilized in open vats (7, 24, 61, 73), but the difficulties increase apace as the goal of half-second viscosity nitrocellulose is approached, for the pretreatments necessary have tended to injure the fiber structure excessively with attendant processing difficulties and losses in yield (9).

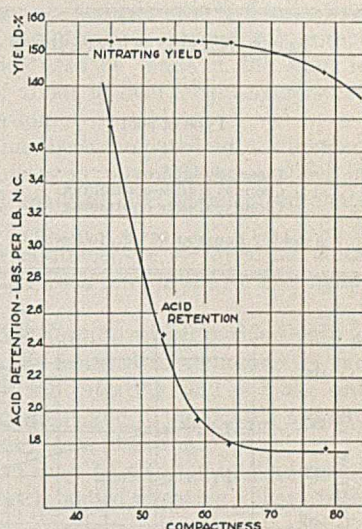


FIGURE 8. EFFECT OF VARYING THE COMPACTNESS OF DRYER BOARD ON NITRATING YIELD AND ACID RETENTION (TWO-ACID PROCESS)

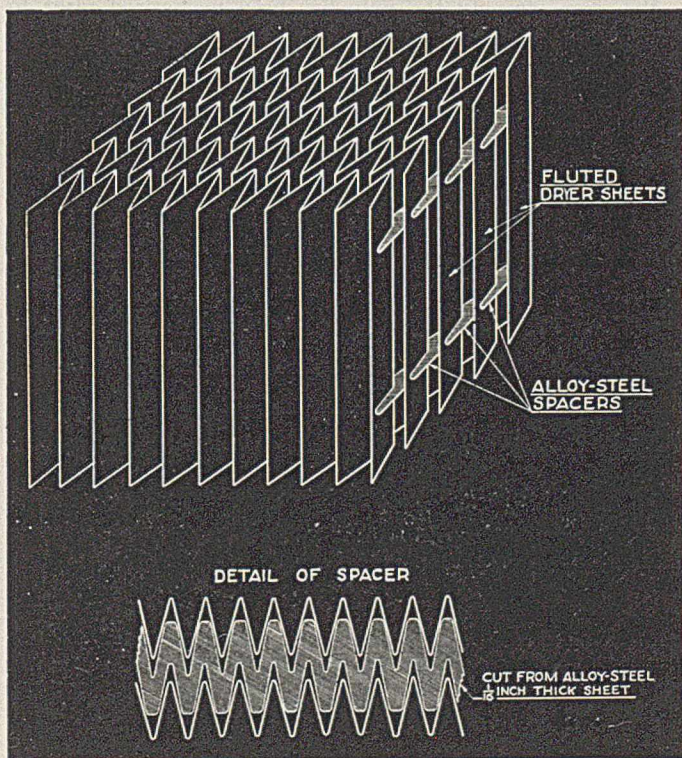


FIGURE 7. METHOD OF FLUTING AND SPACING DRYER BOARDS FOR NITRATION BY TWO-ACID PROCESS

TABLE XXIII. COMPARISON OF RESULTS OBTAINED WITH SLUDGE-FREE AND WITH SLUDGE-CONTAINING MIXED ACIDS<sup>a</sup>

Type of acid	A Acid			B Acid			Nitrating Yield %	Acid Retention, per Lb. Nitrocellulose Lb.	Nitrogen Content %	Grading for Smoothness of Soln.
	H <sub>2</sub> O %	HNO <sub>3</sub> %	H <sub>2</sub> SO <sub>4</sub> %	H <sub>2</sub> O %	HNO <sub>3</sub> %	H <sub>2</sub> SO <sub>4</sub> %				
Clear, sludge-free	19.0	36.0	45.0	18.2	21.0	60.8	162.0	2.18	11.88	Good to good +
Cloudy, sludge-containing	18.4	35.8	45.7	17.2	21.2	61.6	159.8	2.25	11.92	Good to good +
Cloudy, sludge-containing	17.3	36.7	46.0	17.8	20.9	61.3	159.3	2.32	11.92	Good to good +

<sup>a</sup> A acid, 2 hours at 86° F., followed by B acid for 4 hours at 104° F.; pulpboard, basis weight 250, compactness 60.

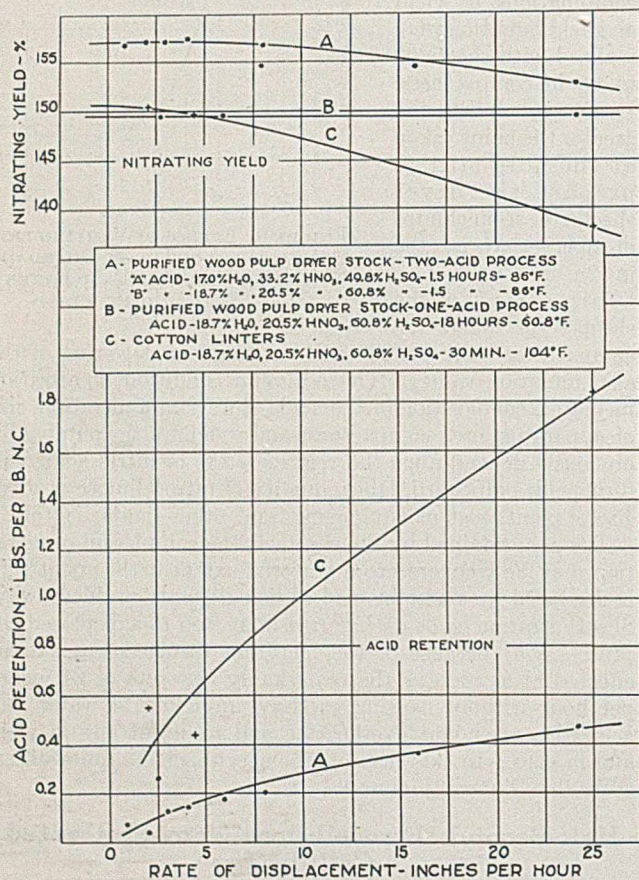


FIGURE 9. REMOVAL OF RETAINED NITRATING ACID BY DISPLACEMENT WITH WATER

An exception, in a sense, is the nitration of deglycerolated scrap Cellophane (14), but in this case the cellulose is in a nonfibrous condition. The desired results with pretreated fiber may, however, be realized according to an interesting method developed by the Brown Company, which has been practiced on a semi-works scale with satisfactory results. In brief, the procedure comprises treating sheets of interfelted cellulose fibers with viscosity-lowering reagents, washing and drying the sheets while maintaining them intact, and nitrating the treated fibers in sheet form (54). Because the

stock has been conditioned and nitrated in interfelted condition, the fines generated by the pretreatment or during nitration are retained; hence the yield of nitrocellulose is high and the viscosity of the finished product is low. For example, sheets of purified wood pulp weighing about 30 grams per square foot and about 0.030 inch thick are steeped in 17 per cent sodium hydroxide solution at room temperature for a few seconds, then are passed through squeeze rolls into boiling water and washed nearly free from sodium hydroxide with several changes of warm water. The sheets are then boiled 60 minutes in a solution containing one per cent free sulfuric acid, after which they are washed until neutral, resqueezed by passage through rolls, and dried on a drum dryer. Upon nitration by the two-acid method previously described the boards yield about 158 per cent nitrocellulose with a nitrogen content of 11.9–12.0 per cent and a solution viscosity of half-second. Solutions of the nitrocellulose are clear and homogeneous, and are as free from coloring matter as the best half-second nitrocellulose commercially available.

Although pretreatment of the cellulose with either sodium hydroxide of mercerizing strength or with acid alone reduces the solution viscosity of the final nitrocellulose markedly, by far the best results have been obtained with mercerization followed by hydrolysis (41). The reasons for this phenomenon are somewhat obscure but are probably related to the observation that the nitrocellulose viscosity is generally lower for a given cuprammonium viscosity of the cellulosic raw material the more strongly the pulp has been mercerized prior to nitration.

Atsuki (4) found that cellulose recovered from nitrocellulose formed from mercerized cotton has a higher copper number than cellulose recovered from nitrocellulose made from normal cotton, despite the fact that the copper numbers of the mercerized and normal cottons used in nitration were the same. This observation is interpreted to mean that mercerized

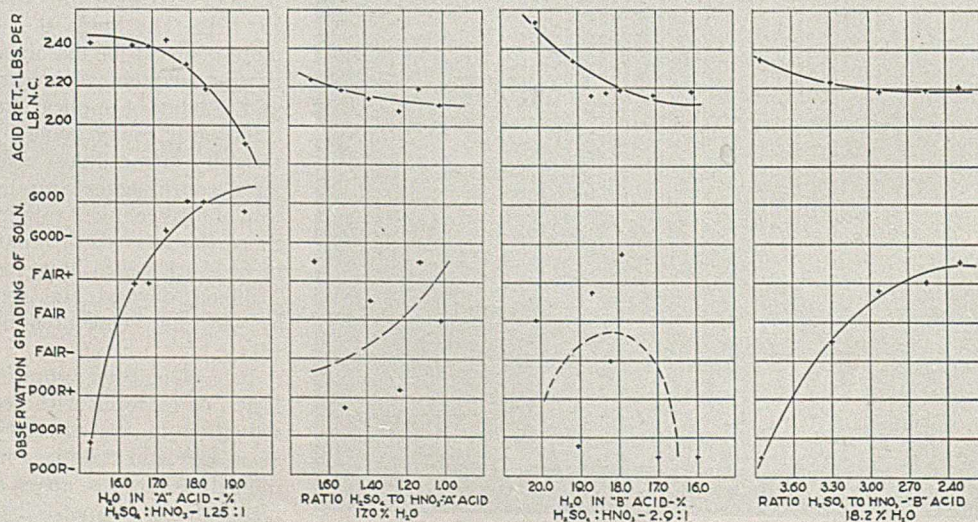


FIGURE 10. EFFECT OF VARYING THE ACID COMPOSITION UPON ACID RETENTION AND PRESENCE OF "FISH EYES" IN SOLUTIONS OF NITROCELLULOSE (TWO-ACID PROCESS)



cotton cellulose is modified more during nitration than is the normal cotton cellulose. He reports that nitrocellulose from mercerized cotton gives a higher solubility, lower viscosity, and higher sulfuric acid content than that from normal cotton. The sulfuric acid retained by the nitrated mercerized cotton is easily eliminated by boiling; hence mercerization has little effect on the stability of the corresponding nitrocellulose.

Departure from the usual nitrating procedure was adopted in the two-acid nitration of pretreated dryer sheets when it was discovered that the clearest nitrocellulose solutions in the customary solvent mixtures are obtained if the nitrated sheets are drowned in water at 40° C. (104° F.) rather than in unheated water (58). No serious loss in yield of nitrocellulose results from the elevated temperature of the drowning water (Table XXIV).

TABLE XXIV. EFFECT OF TEMPERATURE OF DROWNING ON NITRATING YIELD AND CLARITY OF NITROCELLULOSE SOLUTION<sup>a</sup>

No.	1	2	3	4	5
Drowning temp., ° F.	68	86	104	122	140
Temp. rise in drowning bath, ° F.	16.2	12.6	9.0	9.0	9.0
Nitrating yield, %	158.4	158.4	157.0	153.8	147.5
Condition of nitrate soln.	Smooth and fairly clear	Smooth and clear, not as clear as No. 3	Smooth and clear, best in clarity	Smooth and slightly hazy	Granular and hazy

<sup>a</sup> Pulp used: mercerized hydrolyzed pulpboards, basis weight 200, compactness 57; acids used: A acid, 15.8% H<sub>2</sub>O, 36.6 HNO<sub>3</sub>, 47.6 H<sub>2</sub>SO<sub>4</sub>, 2 hours at 86° F.; B acid 17.8% H<sub>2</sub>O, 21.5 HNO<sub>3</sub>, 60.7 H<sub>2</sub>SO<sub>4</sub>, 4 hours at 100° F.

Films of the nitrate prepared from the mercerized hydrolyzed dryer sheets nitrated as described were normal in tensile strength and in flexing endurance. Solutions and films likewise responded normally to heat and to light exposures. These facts are significant, especially since alpha-cellulose determinations on samples of the nitrated stock and on commercial half-second nitro cotton denitrated by treatment with an aqueous solution of ammonium sulfide indicate a greater content of nitrated hydrocellulose in the wood pulp product.

Significant also is the relatively high yield and the high stability of the nitrated cellulose prepared from the mercerized and hydrolyzed wood cellulose, the alpha-cellulose content of which is lowered by the pretreatment from an initial value of about 95 down to about 70 per cent.

### Nitration of Flaked or Peeled Pulpboard

In the writers' earliest work on the nitration of wood pulp, they reduced commercial sulfite pulpboard by hand into thin flakes or peelings. This is quite readily done because the fibers, for the most part, lie parallel to the surface of the board. The peelings nitrated quite satisfactorily with the usual nitrating acids, for yields of about 145 per cent were obtained in the use of nitrocellulose containing about 11 per cent nitrogen; the nitrocellulose was almost completely soluble in the usual solvents to give sparkling, clear solutions. The time of nitration was normal for the pot process (about 30 minutes); the temperature of nitration was about 105° F. These results are most significant but, because the results were not quite as good as those obtained with cotton or with purified wood pulp otherwise more acceptably handled by the industry as a whole, the matter was not pursued to the stage of designing a machine to reduce pulpboard into flakes or peelings on a commercial scale.

### Conclusions

1. Properly refined wood fiber yields stable nitrocellulose as free from coloring matter as the nitrocellulose obtained from the best commercial grades of cotton fiber.

2. When the customary commercial method of nitrating cotton linters is applied to the nitration of wood pulp, practically no change in practice need be made if the pulp is shredded in the presence of about its own weight of moisture and is redried prior to nitration.

3. Purified wood fiber has been prepared in a shredded form closely resembling linters in physical appearance, in response to usual chemical analyses, and in nitrating characteristics.

4. Customary nitrating equipment and nitrating acids give good results with purified wood pulp in the form of light-weight paper.

5. Pulpboard, the cheapest form in which purified pulp is commercially available, can be nitrated to advantage in the usual nitrating apparatus if the nitrating acid is made unusually rich in nitric acid content and if the boards are cut into small pieces before nitration.

6. Pulpboard may be nitrated in the form of large sheets, but modified nitrating apparatus is then necessary.

7. The displacement method of removing spent acid from the nitrated cellulose can be applied to advantage when relatively large sheets of pulpboard are nitrated in a properly stacked condition.

8. So-called half-second nitrocellulose of excellent quality may be prepared direct by the nitration of pretreated sheets of wood pulp.

9. Such nitrocellulose is normal in stability, despite the fact that the alpha-cellulose content of the conditioned wood pulp prior to nitration may be as low as 70 per cent.

10. Pulpboard gives promising results with the usual nitrating equipment and acids when flaked or peeled into thin laminae prior to nitration.

TABLE XXV. DATA OBTAINED IN NITRATION OF SMALL PIECES OF PULPBOARD<sup>a</sup>

Basis weight of pulpboard	188	188	134	134
Compactness of pulpboard	66	66	77	77
Compn. of nitrating acid, %:				
H <sub>2</sub> O	12.86	14.87	12.86	14.87
HNO <sub>3</sub>	44.38	43.09	44.38	43.09
H <sub>2</sub> SO <sub>4</sub>	42.76	42.04	42.76	42.04
Ratio weight of nitrating acid to weight of pulp	10:1	10:1	10:1	10:1
Nitration temp., ° F.	104	104	104	104
Nitration period, min.	45	45	45	45
Acid retention, lb./lb. nitrocellulose	1.41	1.53	1.37	1.42
Nitrating yield, %	155.2	149.0	155.8	151.7
Nitrogen content, %	11.95	11.00	11.86	11.06
% of theoretical yield	95.5	96.3	96.5	97.8
Clarity of nitrocellulose soln.	Very good	Very good	Very good	Very good

<sup>a</sup> In the form of 0.25-inch squares.

### Nitration Procedures

**POT PROCESS.** Weigh 30.0 grams of pulp previously dried one hour at 105° C. into a tared aluminum can provided with an air-tight cover, and permit to cool in a desiccator. Pour 1500 grams of mixed acid into a 1.5-liter beaker, carefully warm to 40.0° C., and set the beaker in a constant-temperature bath maintained at 40.0° ± 0.2° C. Transfer the pulp sample to the beaker and stir the acid rapidly with a thermometer to immerse the fiber as quickly as possible. Continue the stirring for one minute and note the temperature rise to within 0.1° C. Thirty minutes after the pulp has been added to the acid, pour the mixture into the tared aluminum centrifuge pot (Figure 12) and centrifuge for one minute at 1800 r. p. m.

During the centrifuging, rinse the emptied beaker in the bath, to be used later in drowning the centrifuged nitrocellulose. The container for the drowning water conveniently consists of a box with a capacity of about 50 liters, provided with a bottom drain fitted externally with a rubber stopper. A sheet of nainsook is loosely hung around the inside of the box to provide a draining surface.

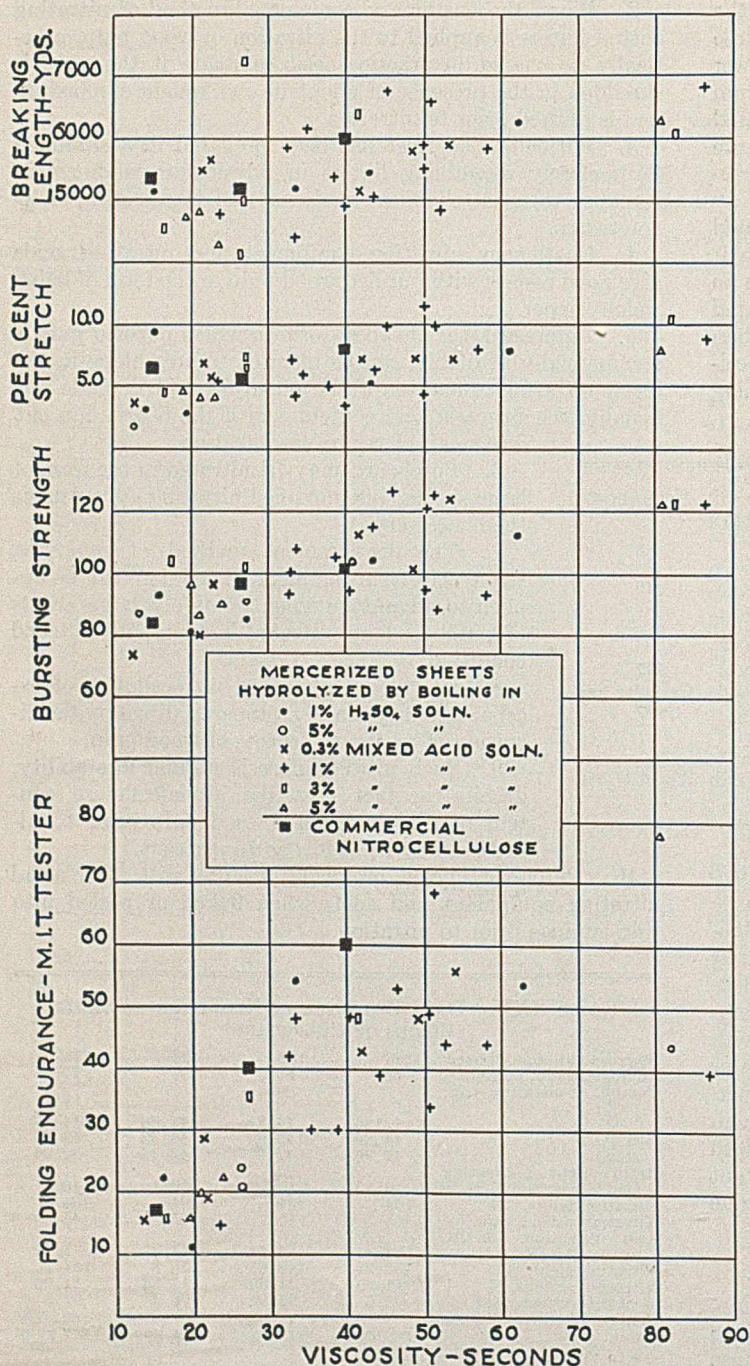


FIGURE 11. COMPARISON OF FILM CHARACTERISTICS OF COMMERCIAL HALF-SECOND NITROCELLULOSE WITH LOW-VISCOSITY NITROCELLULOSE PREPARED FROM MERCERIZED HYDROLYZED DRYER BOARDS (TWO-ACID PROCESS)

After the nitrocellulose has been centrifuged one minute, remove the centrifuge pot from the machine, weigh, and quickly transfer the nitrated fiber to the drowning bath. The water in the bath should be about 20° C. Thoroughly rinse the centrifuge pot free from nitrocellulose and acid.

Wash the nitrated fiber with several changes of water until the desired acidity is attained, then transfer the drained fiber to a liter of boiling distilled water and continue the boiling one hour if only yield, acid retention, and color of nitrocellulose are desired; otherwise extend the time of boiling as desired. At the end of the boiling, return the sample to the drowning box and wash on a nainsook cloth with cold water until the sample is neutral to bromothymol blue. Drain and squeeze out the excess water, then spread the nitrated fiber on an aluminum tray and dry overnight in an oven at 45° to 50° C., through which a lively draft is maintained.

$$\text{Per cent yield} = \frac{\text{Dry weight of nitrocellulose} \times 100}{30}$$

$$\text{Acid retention} = \frac{\left( \text{Weight of acid-wet nitrocellulose after centrifuging} \right) \text{ minus } \left( \text{dry weight of nitrocellulose} \right)}{\text{Dry weight of nitrocellulose}}$$

*Notes.* Ordinarily, distilled water is used throughout the procedure. The bulk of the experimental work done in the Brown Company laboratories was in connection with nitrocellulose of the pyroxylin type. The composition of the mixed acid was 18.7 per cent water, 20.5 per cent nitric acid, and 60.8 per cent sulfuric acid. The acids used in the laboratory were ordinarily of the so-called technically pure grade.

**TWO-ACID SHEET PROCESS.** If the sample is in bulk form, make up hand-sheets of 220-230 pound basis weight and 55-60 compactness. Cut the sheets into pieces 7.62 × 10.16 cm. (3 × 4 inches) and punch holes in each piece, as shown in Figure 13, for convenience in hanging on the metal rack. Dry a sufficient number of the small sheets one hour at 105° C. to give approximately 30 grams of cellulose. Determine the exact bone-dry weight and suspend on the rack, alternating sheets with spacers. Determine the combined weight of the rack, the spacers, and the sheets.

After drying the assembly at 105° C. for 15 minutes, cool in a desiccator, and then submerge in a weight of the A acid at 30° C. equal to fifty times the weight of the sheets. Maintain the temperature of the acid 30° ± 1° C. After the reaction has proceeded for 3 hours, lift the rack and sheets out of the acid, allow to drain 10 seconds, and transfer to the B acid at 40° C. Adjust the weight of acid in the bath until the total quantity surrounding the sheets is equal to fifty times the weight of the original pulp. Maintain the temperature of the B acid 40° ± 1° C. After the fibers have been in contact with the B acid for 3 hours, remove the rack assembly, allow it to drain 10 seconds, and then drown it in a liter of water. The water temperature should be 20° C. if the nitrocellulose is of the 4-second or higher variety; if the nitrocellulose is of the half-second or lower type, the drowning-water temperature should be 40° C. After the sheets have been soaked 5 minutes, wash them twice by decantation, at 20° C. if the drowning water is initially at 20° C., and at 50° C. if the drowning water is initially at 40° C.

Transfer the rack assembly into a liter of boiling water and boil one hour or longer, as desired. Usually the acidity of the stabilizing bath should be 0.1 to 0.2 per cent, figured as sulfuric acid, at the completion of the boil. Wash the boiled sample with water at room temperature until the nitrocellulose is neutral to bromothymol blue. Remove the sheets, squeeze out excess water, place on an aluminum tray, and dry overnight in an oven at 45-50° C. through which a lively draft is maintained.

*Notes.* Wherever acid retention figures are given in the tables for the two-acid process, they were determined by weighing the rack assembly after it had been removed from the B acid and drained. The figures thus obtained manifestly tell only a part of the story, for the retained acid is obviously a mixture of spent A and B acids.

**DETERMINATION OF FREE ACID IN NITROCELLULOSE.** Dry the nitrocellulose at 50° C. overnight. Dissolve 10.0 grams in 300 grams of a 90 per cent acetone-water solution made up by weight from redistilled acetone and distilled water. Add 1.0 cc. of bromocresol green indicator and titrate with 0.02 N sodium hydroxide to a pH of 4.8. Determine the end point by matching the sample during titration with a standard prepared by adding the indicator to 300 cc. of distilled water brought to a pH of 4.8. Report the acidity as parts per million of sulfuric acid based on the dry nitrocellulose.

*Notes.* Run a blank titration on the acetone-water mixture used as solvent. Adjust the indicator before use to a pH of 4.8. The foregoing method for determining acidity was devised by the Du Pont Viscoloid Company, after a study of the paper by Cray and Westrip (15). Acknowledgment is gratefully made of the permission granted by the Du Pont Viscoloid Company to include the procedure in the present article.

**VISCOSITY OF NITROCELLULOSE IN SOLUTION, STABILITY OF NITROCELLULOSE.** These procedures are essentially the same as those given by the Hercules Powder Company (23A). In the case of the determination of the viscosity of nitrocellulose of

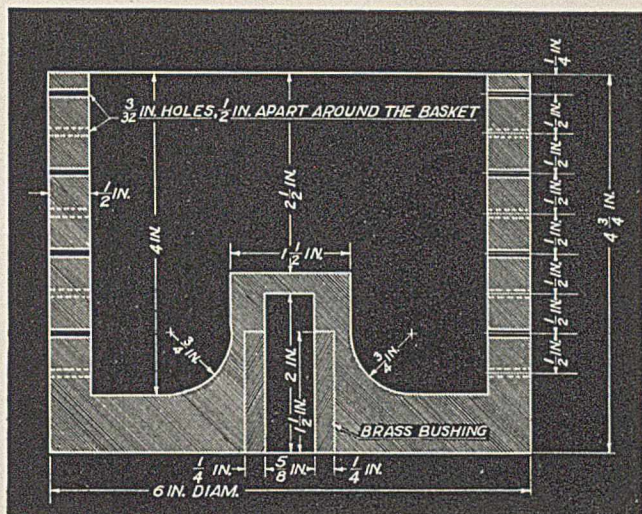


FIGURE 12. CROSS SECTION OF CAST-ALUMINUM CENTRIFUGAL BASKET USED IN THE LABORATORY

the half-second type, the sizes of the viscometer tube and steel ball are modified. A tube 1.9 cm. (0.75 inch) in internal diameter and 38 cm. (15 inches) long, and a steel ball 0.15 cm. (0.059 inch) in diameter are used. The tube is marked off 5.1 cm. (2 inches) from the top and 7.6 cm. (3 inches) from the bottom. The viscosity is reported in seconds for the ball to drop between the two marks, a distance of 25.4 cm. (10 inches). Commercial half-second nitrocellulose by this modified method has a viscosity of 25 to 50 seconds.

**COLOR OF NITROCELLULOSE.** Dissolve 2.0 grams of the dry nitrocellulose in 100 cc. of redistilled acetone and pour into a Nessler tube to a depth of 12.7 cm. (5.0 inches). Determine the "color" of the acetone solution by noting the depth of a standard potassium iodide-iodine solution in a similar tube which matches most closely the sample.

Consider 1.27 mm. (0.05 inch) depth of the potassium iodide-iodine standard equivalent to one point of color. The Nessler tube used for the standard solution is conveniently graduated in tenths of an inch.

Prepare standard potassium iodide-iodine solution daily by diluting 1 cc. of a stock potassium iodide-iodine solution with 400 cc. of distilled water. The stock solution consists of 1.00 gram of resublimed iodine and 10.0 grams of potassium iodide in 300 grams of water.

**PHYSICAL CHARACTERISTICS OF FILM.** Dissolve the nitrocellulose in a mixture of 25 per cent 2-B denatured alcohol, 20 per cent ethyl acetate, and 55 per cent toluene by weight. As in the case of the viscosity measurements, make up 20 per cent solutions by weight of half-second nitrocellulose, and 12.2 per cent solutions of 4-second and higher material.

Cast films with a scraper blade having a clearance of 0.89 mm. (0.035 inch). As soon as the solution has been spread, dry it 5 to 7 hours in a box through which air, previously bubbled through sulfuric acid (specific gravity, 1.84), is passed at room temperature. Remove the film and further dry 48 hours at 50° C. in an oven through which a lively draft of air is maintained. The tests are as follows:

**Basis Weight.** The basis weight is equivalent to (914.3 times the weight in grams) divided by the area in square inches.

**Compactness.** The compactness is equivalent to the basis weight divided by (100 times the thickness in inches).

**Bursting Strength (Mullen or Pop Test).** The values for bursting strength given in Figure 11, were determined with a modified motor-driven Mullen tester and represent the pressure in pounds per square inch necessary to rupture a circular area of the film 12.7 mm. (0.500 inch) in diameter, the pressure increasing at the rate of 5 pounds per square inch per second.

**Folding Endurance.** The testing machine used has already been described (68A).

**Tensile Strength, Breaking Length, Per Cent Stretch.** The testing

machine used is the Schopper tensile breaking strength tester (68B).

Note. All films were seasoned overnight at 70° F. and 45 per cent relative humidity before being tested.

## Pulp and Paper Tests

The pulp and paper tests used are essentially those compiled by Richter (40).

**3 PER CENT SODA SOLUBILITY.** In earlier work on the purification of wood pulp for nitration, the so-called 3 per cent soda-soluble test was used. Briefly, it comprises boiling a finely shredded sample of pulp in a 3 per cent sodium solution for one hour, and determining the percentage of the sample dissolved. The color of the caustic liquor drained from the pulp at the end of the boil is a rough indication of the degree of purity of the cellulose, the darkest colors being obtained with the most impure pulps.

**7.14 PER CENT SODA SOLUBILITY.** This test is similar to the 3 per cent soda-soluble test except for the strength of the caustic solution and for the time of boiling, which is 3 hours instead of 1 hour. It is the method adopted by the nitrating industry as a measure of the purity of the cellulose raw material.

**COLOR OF PULP.** The method for determining the color of pulp is practically that described by Van Arsdell (70).

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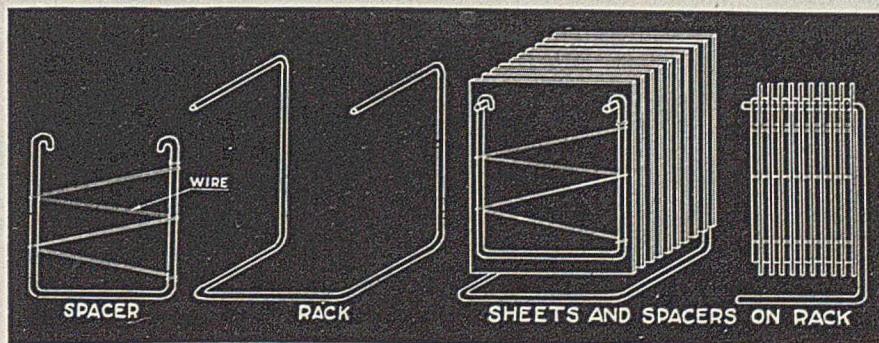


FIGURE 13. METHOD OF HANDLING DRYER BOARD IN THE LABORATORY BY TWO-ACID PROCESS



PORTION OF  
WOOD CHIP  
LOFT IN  
DIGESTER HOUSE

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# Nature of Cigaret Smoke

## Volatile Bases and Acids<sup>1</sup>

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Aside from the nature of the aromatic substances present, cigaret smoke is characterized by its volatile base content and the proportion of acids to bases. The basic and acidic constituents of smoke are related to the composition of the tobacco from which it is derived. These relations are altered by changes in physical properties and smoking environment, as they influence the combustion of the finished cigaret.

Methods for the analysis of tobacco and smoke are outlined, and precise methods for the determination of volatile bases, volatile acids, nicotine, and formic acid are described in detail. Data on several types of cigarets are given, and the significance of some chemical and physical properties is indicated.

**R**EPORTED chemical analyses of tobacco smoke have been concerned chiefly with two objectives: the correlation of tobacco quality with the constituents of smoke and the determination of its physiologically active constituents. The present research undertakes to point out certain characteristics which influence the palatability of smoke and to associate these with the chemical and physical properties of the cigaret from which the smoke is derived.

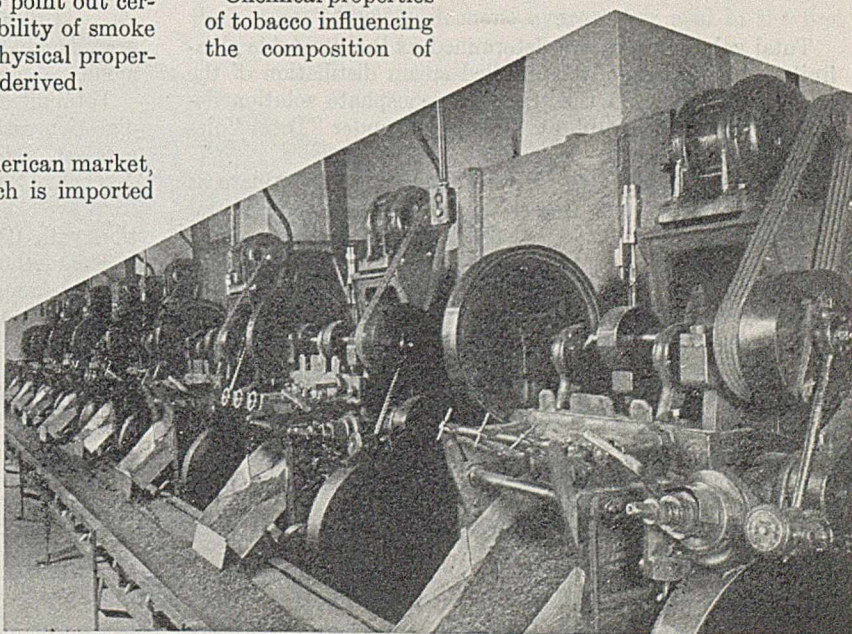
### Cigaret Tobacco

In the blending of cigaret tobacco for the American market, four major types predominate: Turkish, which is imported from Turkey and neighboring countries, and the three domestic types, Bright, Burley, and some Maryland to enhance combustion. Subtypes are designated according to their geographical origin and each bears the stamp of its own locality in certain distinguishing characteristics. Subordinate to the main geographical types are the "markets" in the case of domestic tobacco and the "villages" in the case of Turkish. In these the differences are distinguishable but not so great as between main subtypes. Aside from differences in variety of seed, soil, climatic conditions, and culture, the major types possess quite different char-

acteristics by virtue of the methods of curing. Bright tobacco is flue-cured—that is, dried quickly by artificial heat which fixes quantities of reducing sugars in the leaf. Burley and Maryland types are slowly air-cured or dried, with the resultant degradation and loss of practically all of their reducing sugars. Turkish tobaccos are sun-cured, which results in a partial degradation of carbohydrate material. The subtypes vary from almost a Burley to a Bright-like type.

Within these geographical groups the expert defines his grades, relying principally on certain recognizable physical characteristics such as color, texture, thickness, elasticity, and "grain." Much of the chemical investigation of tobacco has been hampered by the lack of any primary reference standard of quality. But by extensive chemical analyses of various types carefully graded by leaf experts, an accurate evaluation of the various grades has been made. Large variations are found, not only between different types, but within each type, depending upon geographical origin, position on the stalk, and climatic and soil conditions. Skillful blending is required to combine the good features of each type to produce a palatable cigaret. The analysis of smoke produced from these various types has made it possible to define the characteristics of smoke in terms of its chemical composition and to relate these characteristics to the composition of the tobacco from which it is produced. Fundamentally, the character of smoke depends upon the aromatic substances produced on pyrolysis of the resinous material peculiar to each of the tobacco types, and the base content, as tempered by the proportional quantity of acids present.

Chemical properties  
of tobacco influencing  
the composition of



GUILLOTINE CUTTING MACHINES WHERE THE LEAF BLEND IS CUT INTO SHREDS FOR CIGARET MANUFACTURE

<sup>1</sup> The first article in this series appeared in July, 1936 (6).

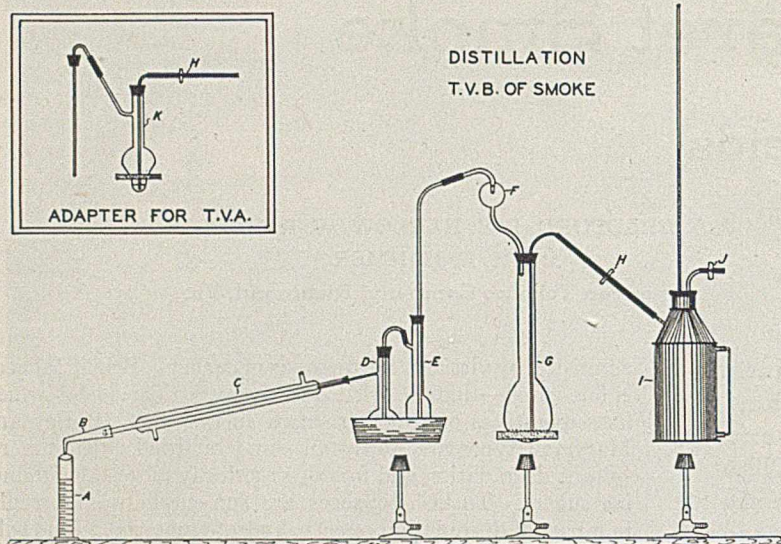


FIGURE 1

cigaret smoke are: the nitrogen content and its distribution among the various forms, principally nicotine and the easily liberated ammonia; the carbohydrate content, including both the naturally occurring and added sugars; and the ash content, which to some extent serves as an index to combustibility in domestic tobaccos.

Table I shows chemical analyses of a representative grade of each of the three major cigaret types.

TABLE I. ANALYSES OF REPRESENTATIVE TYPES OF CIGARET TOBACCOS (IN PER CENT MOISTURE-FREE TOBACCO)

Tobacco Type	Total N as NH <sub>3</sub>	Protein N as NH <sub>3</sub>	T. V. B. <sup>a</sup> as NH <sub>3</sub>	Nicotine	T. V. B. minus Nicotine as NH <sub>3</sub>	Ratio, Nicotine as NH <sub>3</sub> to T. V. B. as NH <sub>3</sub>	Reducing Sugars as Dextrose	Ash
Bright	2.22	0.69	0.391	2.58	0.120	0.69	20.4	14.3
Burley	3.87	1.57	0.650	2.90	0.345	0.47	<1.0	23.4
Turkish	2.56	1.26	0.302	1.13	0.183	0.39	12.2	17.3

<sup>a</sup> Total volatile bases.

Total volatile bases are determined as the titratable alkalinity after a carefully controlled steam distillation of the tobacco sample from the trisodium phosphate solution described in the paragraph on "Reagents" under "Total Volatile Bases."

Nicotine is precipitated in an aliquot of this distillate as recommended by the Association of Official Agricultural Chemists (2).

Total nitrogen is determined by the Kjeldahl-Gunning-Arnold method (1) as modified to include the nitrogen of nitrates.

The tobacco extract for the sugar determination is prepared according to Schmuck (19). The A. O. A. C. method is followed for the copper reduction (3).

Ash is determined by heating the sample at 450° to 500° C. in a muffle to constant weight.

It is apparent from Table I that the relative proportion of nitrogen and carbohydrate constituents varies extensively in different types of tobacco. Comparatively, the air-cured tobaccos are high in volatile nitrogenous constituents and ash, but low in reducing sugars; the flue-cured tobaccos are relatively high in reducing sugars and low in volatile nitrogen and ash. Turkish is intermediate in chemical composition between the Bright and Burley types.

When the part that such physical properties of a cigaret as

weight, size, moisture content, etc., play in modifying the conditions of combustion is recognized, a general relation is found between the constituents of tobacco and its smoke. It has been found possible, in most instances, to relate changes in taste, irritation, and apparent strength to alteration in smoke composition.

### Smoke Bases

The presence in tobacco of nicotine and related alkaloids, with other nitrogenous compounds which are not found to any great extent in other leafy material, has focused the greatest attention on the bases of smoke. Schmuck (19) enumerates the probable nitrogen compounds in cigaret smoke as nicotine, ammonia, simplest amines, pyridine bases, and pyrrole derivatives. Gavrilov and Koperina (9) found in the types they studied a high base content in tobaccos they described as harsh and strong, together with a decrease in the ratio of nicotine to total nitrogen as quality diminished. Hall and Earl (13) concur on this point, and note that a high base content in smoke may be compensated for by sufficient neutralizing acids.

The transfer of a portion of the nicotine in tobacco to its smoke is now generally accepted. At one time reports were conflicting, but the preponderance of concordant chemical and biological evidence has definitely established the presence of considerable amounts of the unchanged alkaloid (7, 11, 18, 20). Jensen and Haley (14) studied the silicotungstic acid method for the determination of nicotine, and demonstrated that pyridine did not interfere. The identity of the insoluble silicotungstate of smoke distillate with nicotine silicotungstate has been established in this laboratory by mixed melting points of the picrates and picrolonates of the regenerated base. This has been confirmed by determining the loss in weight on ignition of the well-dried precipitate. The silicotungstic acid method for nicotine has been adopted as standard. Bio-assays of smoke for nicotine must be qualified, since Haag (10) has shown that the animal susceptibility to smoke preparations exceeds what would be expected from the nicotine content alone.

Total nitrogen is determined in smoke by a slow and careful digestion with sulfuric acid, potassium sulfate, and a mercury catalyst. Half of the quantities recommended by the A. O. A. C. (1) are sufficient for the digestion of the smoke from five cigarets. A sample of this size is adequate for titration with 0.025 N reagents.

The method of Vickery and Pucher (21) for the determination of ammonia was shown by them to be free from interference of other bases. Haley, Jensen, and Olson (12) reported the successful adaptation of the method to the analysis of cigar smoke, and it has proved equally satisfactory for cigaret smoke.

Barta and Toole (5) calculate the ammonia in smoke as the difference between the total volatile bases and the alkalinity due to nicotine. Although this quantity is of much greater magnitude than the true ammonia content, it is nevertheless valuable in describing both tobacco and smoke. It is roughly proportional to the true ammonia, although the factor of proportionality varies in different types of tobacco. Either the compounds in the tobacco yielding this additional ammonia or very similar ones are transferred to the smoke stream.

Pyridine is of interest principally because of the attention

it has received in the literature. Because of its weak basicity, and the solubility of its silicotungstate, it is not included quantitatively with the volatile bases or nicotine. The microcolorimetric method of Kulikov and Krestovosdvienskaya (15) was found to be sensitive to 0.02 mg. of pyridine, without interference by such compounds as pyridine homologs, piperidine, quinoline, pyrrole, and nicotine.

### Smoke Acids

Although the presence of acids in tobacco smoke is expected from the nature of the material and its pyrolysis, and has been occasionally reported, their significance has not been generally recognized. This is partially attributable to the fact that they have been overshadowed by the physiologically active smoke bases.

Several investigators have demonstrated the presence of volatile organic acids in tobacco smoke. Neuberg and Burkard (17) report the identification of formic, acetic, and butyric acids in smoke. Lehmann (16) indicates their presence and suggests a method for their determination. Gabel and Kipriyanov (8) have identified formic, acetic, and propionic acids in the distillate of destructively distilled tobacco. Hall and Earl (13), in work on Australian tobacco, state that smoke from good tobaccos is generally neutral or slightly acid, and that from bad tobaccos is usually definitely alkaline. This, of course, applies particularly to Australian tobacco, for Wensch (22) has found that different types of tobacco of good quality yield different degrees of acidity in the smoke. Oriental, Virginia, and similar Bright types give rise to an acid smoke; that from cigar tobaccos and Burley types is alkaline.

Both formic and acetic acids have been identified in cigarette smoke in this laboratory. Formic acid is quantitatively estimated from the amount of mercurous chloride formed by treatment of the smoke distillate with mercuric chloride, sodium acetate, and hydrochloric acid. The bulk of the remaining acidity is due to acetic acid.

### Total Volatile Bases

The essentials of the proposed method of determining volatile bases and nicotine are to control the distillation to recover completely the nicotine with minimized hydrolysis, and to absorb the bases in hot standard acid, allowing the greater portion of the aqueous distillate to escape. In this way carbon dioxide is eliminated, the final volume is small, and a sharp end point is found with the dilute titrating solutions used.

**APPARATUS.** The still is shown in Figure 1. Steam generator *I* carries a safety tube and bleeder, *J*, to control the pressure. Screw cock *H* controls the rate of admission of steam to boiling flask *G* (300-cc. Kjeldahl flask used in smoke collection) containing the alkalinized smoke sample. An asbestos board with a 2-inch (5-cm.) hole covered with a wire gauze protects the exposed sides of flask *G* against drying. The distillate passes through spray trap *F*, and into standard sulfuric acid in *E* and *D*, where the bases are absorbed. The alcohol and water vapor are condensed in *C*, pass through adapter *B* into graduate *A* where they are measured to control the distillation rate. The contents of absorbers *E* and *D* are maintained constant by heating the glycerol bath in which they rest; a temperature of about 115° C. is usually sufficient.

**REAGENTS.** The approximate reagents are 0.5 *N* alcoholic hydrochloric acid, 0.5 *N* aqueous hydrochloric acid, 2.5 *N* aqueous sodium hydroxide, 1 per cent methyl red in 50 per cent alcohol. The standard reagents are 0.025 *N* sulfuric acid, 0.025 *N* sodium hydroxide, trisodium phosphate solution (contains 58.67 grams anhydrous trisodium phosphate and 3.33 grams sodium hydroxide per liter). Preparation is as follows: 133.3 grams of c. p.  $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$  are dissolved in distilled water and made to 1 liter. After clearing, an aliquot is titrated to phenolphthalein and then to methyl orange, using the point of maximum change as end point:

Cc. to phenolphthalein end point =  $\text{NaOH} + \frac{1}{2} \text{PO}_4^{---}$   
Cc. phenolphthalein to methyl orange =  $\frac{1}{2} \text{PO}_4^{---}$

The solution is then adjusted to the proper concentration and checked by titration. Adjustment of either the  $\text{Na}^+$  or  $\text{PO}_4^{---}$  content, or both, may be necessary, since there is some variation in the alkalinity of c. p. trisodium phosphate. This is accomplished by adding the required quantity of orthophosphoric acid or sodium hydroxide.

### Smoking

The smoking apparatus and technic have been described (6). For collecting bases, 1 cc. of 0.5 *N* alcoholic hydrochloric acid and 10 cc. of alcohol are placed in the tared collection flask, 5 cc. of 0.5 *N* alcoholic hydrochloric acid in the first

### PACKING MACHINES

On the making floor, cigarettes are made, automatically counted, and packed. Internal revenue stamps are affixed, and the packs are wrapped in Cellophane.



bubbler, and 5 cc. of 0.5 *N* aqueous hydrochloric acid in the second. The samples of five representative cigarets are weighed and marked 23 mm. from the butt end. Using a 35-cc. puff lasting 2 seconds and taken once a minute, the cigarets are smoked to the mark and the number of puffs is recorded.

### Distillation

After settling for 20 minutes, all portions of the collection apparatus are washed into the flask with a minimum of hot water and alcohol, used alternately. Sufficient 2.5 *N* sodium hydroxide is added to neutralize the hydrochloric acid used in collection, the contents are made to 80 grams, and the flask is placed on the still. Fifteen cubic centimeters of the 0.025 *N* sulfuric acid are apportioned between absorbers *E* and *D*, about 12 cc. in *E*. Fifteen cubic centimeters of trisodium phosphate solution are added to the Kjeldahl flask, and the apparatus is connected. When the glycerol bath is hot, concentration is begun. Seventy cubic centimeters of distillate are collected in exactly 23 minutes. Steam is admitted, and concentration continued until 20 cc. remain. This volume is maintained while 130 cc. of distillate are collected at the prescribed rate of 2.5 cc. per minute. The contents of the absorbers are washed into a 250-cc. Erlenmeyer flask, cooled to room temperature, and titrated in the presence of methyl red with 0.025 *N* sodium hydroxide to the point of maximum change. A blank is determined on the reagents used. Nicotine is precipitated in the distillate with silicotungstic acid according to the A. O. A. C. (2).

Although the conditions of distillation mentioned appear somewhat arbitrary, they are prescribed by the nature of the smoke mixture and the dimensions of the apparatus. A fairly low volume in the boiling flask is essential to the recovery of nicotine; and to reduce the total time of distillation, the concentration is carried out without the admission of steam. The tendency of the alkaline solution to foam forbids a more rapid rate, while concentration below the 20 cc. volume stated so increases the boiling point that ammonia is produced by excessive hydrolysis of nonvolatile nitrogenous compounds. Where these conditions are rigidly adhered to, there is little difficulty in obtaining check results. Duplicate determinations on the same sample of cigarets will not generally vary more than  $\pm 0.1$  cc. from the average.

### Total Volatile Acids

The proposed method for the determination of the total volatile acids and formic acid in tobacco smoke involves the collection of the smoke in alkali; the precipitation of the nicotine present with silicotungstic acid because of its apparent volatility with steam even from tartaric acid solution; the removal of the excess silicotungstic and sulfuric acids and carbon dioxide with barium hydroxide and the subsequent distillation of the smoke solution with steam into hot standard alkali which allows the bulk of the aqueous distillate to escape.

**APPARATUS.** The acid adapter shown in the inset is substituted for Kjeldahl flask *G* and spray trap *F* in Figure 1. In the case of acids, the glycerol bath is maintained at 108–110° C. instead of 115° C. as in the distillation of the bases.

**ADDITIONAL REAGENTS.** The approximate reagents are 0.5 *N* aqueous sodium hydroxide, 2.5 *N* aqueous sulfuric acid, 1 per cent phenolphthalein in 95 per cent alcohol, 12 per cent silicotungstic acid (2), Celite analytical filter aid, 40 per cent c. p. tartaric acid (free from carbon dioxide and volatile acids), and activated charcoal, washed until neutral.

### Preparation of Smoke Solution

In the collection of acids, 1 cc. of 0.5 *N* sodium hydroxide and 10 cc. of alcohol are placed in the collection flask, 5 cc. of alcohol in the first bubbler, and 5 cc. of 0.5 *N* sodium hydroxide in the second. The sample is prepared and smoked as for the determination of bases, except that ten cigarets are used.

After standing 20 minutes, the collection apparatus is washed

thoroughly with hot water and alcohol into a 100-cc. volumetric flask containing 3 cc. of 2.5 *N* sulfuric acid and 4 cc. of 12 per cent silicotungstic acid. The precipitated silicotungstates are allowed to coagulate in a cold water bath for 20 minutes, after which the solution is made to 100 cc. and filtered through a dry filter with the aid of about 1 gram of Celite. The filtrate is neutralized with anhydrous barium hydroxide, using two drops of phenolphthalein as indicator. The excess barium is kept as small as possible. Celite is added as before, and the alkaline solution filtered through a dry filter into a second dry Erlenmeyer flask containing two drops of 40 per cent tartaric acid to neutralize the excess barium hydroxide.

### Distillation of Smoke Solution

An aliquot of 50 cc. of the solution (equivalent to five cigarets) is pipetted into distillation flask *K* to which has been added exactly 5 cc. of 40 per cent tartaric acid. Fifteen cubic centimeters of 0.025 *N* sodium hydroxide are apportioned between absorption flasks *D* and *E*, 10 to 12 cc. in *E*. The apparatus is connected and, after the glycerol bath has reached a temperature of 95° to 100° C., the solution in *K* is concentrated at the approximate rate of 3 cc. per minute for 12 minutes, the temperature in the glycerol bath being allowed to rise slowly to 108° C. When 40 cc. have been distilled over, steam is admitted through screw clamp *H* and the remaining 60 cc. are distilled at the rate of 1.25 cc. per minute. The volume in distilling flask *K* is maintained at approximately 7 cc. during the steam distillation, the flask having been previously marked at this volume. At the completion of the distillation, which consumes 1 hour, the solutions in the absorption flasks are washed into a 250-cc. Erlenmeyer flask with freshly boiled hot water. Ten cubic centimeters of 0.025 *N* sulfuric acid are added, and the solution is filtered with 0.5 gram of activated charcoal to remove any coloration which masks the subsequent titration end point. The filtrate and washings are combined in a 300-cc. Erlenmeyer flask and heated to boiling, after which the solution is titrated with 0.025 *N* sodium hydroxide, using phenolphthalein as indicator. The end point is the first permanent pinkish tinge in the solution. A blank is determined on the reagents used. The conditions described were found to be the least vigorous which would recover, quantitatively, amounts of pure acetic acid comparable to the volatile acid content of cigaret smoke. Duplicate determinations on the same sample of cigarets should check within  $\pm 0.15$  cc. of the mean.

For the determination of formic acid, the distillate, made alkaline with calcium carbonate, is evaporated nearly to dryness on the steam bath and filtered into a 125-cc. Erlenmeyer flask. The mercury reduction is carried out according to the A. O. A. C. (4), except that 0.2 cc. of hydrochloric acid, 2 cc. of sodium acetate, and 4 cc. of the mercuric chloride reagent are used.

Table II illustrates the reproducibility of results obtainable with the smoking technic (6) and methods of analysis described.

TABLE II. DATA ON DUPLICATE ANALYSES

Cigaret	Av. Vol. of Smoke per Cigaret		Total Bases	Total Acids	Silicotungstic Anhydride	Mercurous Chloride
	Base detn.	Acid detn.				
	Cc.	Cc.	Cc. 0.025 <i>N</i>	Cc. 0.025 <i>N</i>	Gram	Gram
A	364	371	6.95	7.85	0.140	0.018
	378	368	7.05	8.10	0.141	0.018
B	364	368	7.08	8.81	0.156	0.022
	350	364	6.71	8.57	0.148	0.022
C	280	280	9.00	6.24	0.170	0.010
	280	291	9.03	6.24	0.168	0.011
D	364	375	6.30	6.80	0.089	0.012
	371	371	6.38	6.87	0.090	0.011

### Chemical Properties

Tables III, IV, and V, respectively, show the tobacco analysis, physical properties, and smoke analysis of four blends of cigarets, representing the three principal cigaret tobacco types and a typical domestic-turkish blend. Correlation of smoke results by different investigators and on many types of cigarets is facilitated when the yield of smoke constituents in a given volume of smoke is calculated. Data so presented have the most significance in studies of cigaret smoke in its relation to human consumption. Calculation



of smoke material on the basis of the dry weight of cigaret smoked is necessary to arrive at such results as the proportion of nicotine or nitrogen of the tobacco transferred to the smoke stream.

The volatile bases of smoke consist almost entirely of nicotine, ammonia, and amines, and account for about half of the total nitrogen. The ammonia is derived from the original ammonia of the tobacco, from pyrolysis of other nitrogenous compounds, and slight hydrolysis during distillation. The column headed "Ammoniacal" (Table V) includes the ammonia and simple amines of the smoke as determined by titration of the distillate from a brief magnesium oxide distillation. The true ammonia is that found by nesslerization of the same distillate after a permutite purification. The other headings of Table V are self-explanatory.

TABLE III. ANALYSES OF TYPICAL CIGARET BLENDS (IN PER CENT MOISTURE-FREE TOBACCO)

Tobacco Type	Total N as NH <sub>3</sub>	Protein N as NH <sub>3</sub>	T. V. B. <sup>a</sup> as NH <sub>3</sub>	Nicotine	T. V. B. minus Nicotine as NH <sub>3</sub>	Ratio, Nicotine as NH <sub>3</sub> to T. V. B. as NH <sub>3</sub>	Total Sugar as Dextrose	Sucrose as Dextrose	Ash
Bright	2.58	1.08	0.416	2.61	0.142	0.66	15.1	1.7	14.1
Burley	4.34	1.76	0.837	3.34	0.486	0.42	2.1	0	18.9
Turkish	3.07	1.35	0.388	1.51	0.229	0.41	8.4	1.0	17.5
Blend	2.95	1.24	0.462	2.48	0.202	0.56	14.6	2.1	15.4

<sup>a</sup> Total volatile bases.

TABLE IV. PHYSICAL PROPERTIES OF TYPICAL CIGARETS

Tobacco Type	Weight Grams	Circumference Mm.	Air Flow <sup>a</sup> Cc./sec.	Moisture, Wet Basis %
Bright	1.07	26.6	29.2	11.5
Burley	0.97	26.6	24.8	12.0
Turkish	1.07	26.8	30.8	11.1
Blend	1.09	26.6	23.7	11.8

<sup>a</sup> At 3-inch (7.6-cm.) water vacuum.

The most striking departures in Table V are the high base and nicotine contents of the Burley and the high acid content of the Bright. In general, the total nitrogen as well as the volatile bases of smoke parallel those of tobacco in quantity and proportion of nicotine. However, because of the leveling action of the combustion process, the differences are less marked in the smoke. The nicotine transferred to the smoke constitutes a surprisingly constant fraction of that contained in the tobacco. Within these ranges, the lower the content

in the tobacco of a substance, the greater is its relative portion appearing in the smoke stream. Pyridine appears in this scheme of smoke analysis in the filtrate from the nicotine silicotungstate precipitate. The amounts present vary from a trace to approximately 1 mg. per liter in the very alkaline smoke.

The most marked difference between the smoke of the various types is found in the relative acidity, as given by the ratio of volatile acids to volatile bases, which is related to the quantity of sugars in the tobacco. These may be the natural reducing sugars of the leaf, or added glucose, invert sugar, or sucrose. Although sugars contribute somewhat to the quantity of smoke acids and increase slightly the proportion of formic acid, their principal function in reducing alkalinity is to inhibit base formation. The alkaline tobaccos are definitely rich in aroma, which contributes to smoke quality when the excessive base formation is restrained. The added sugar seems to be preferential in its action, reducing the ammonia proportionately more than nicotine. The paper in which a cigaret is wrapped yields some acid on combustion. However, the proportion of paper to tobacco is small and relatively constant (about 4 per cent).

The association of the composition of cigaret smoke with taste sensations leads to some generalizations concerning palatability and chemical constituents. When smoke is alkaline or in too high concentration, the bases act as irritants, particularly to the larynx and trachea; they cause a choking sensation and frequently stimulate the cough reflex. Yet, without a sufficient amount of bases, smoke is flat and lacking in character. Nicotine and ammonia are not interchangeable in the base fraction. As the proportion of nicotine increases from the lower extreme, the smoke (weak and somewhat irritating) becomes smoother and more satisfying; as the other extreme is approached, it becomes heady and deficient in flavor and sensibly more acid than would be indicated by the acid-base ratio. These changes may be masked, however, by added flavor or, as in the case of the Turkish cigaret, by the natural aromatics of the tobacco plant. The acid type of smoke, although less noticeable than either excessive or free bases, is described as harsh or sharp. Tongue bite and nasopharyngeal irritation are more noticeable. Formic and acetic acids comprise the greater portion of smoke acids and, through their local irritant action, seem to be responsible for the effects noted.

TABLE V. ANALYSES OF SMOKE FROM TYPICAL CIGARET BLENDS (IN MG. PER LITER OF SMOKE)

Tobacco Type	Total N as NH <sub>3</sub>	T. V. B. <sup>a</sup> as NH <sub>3</sub>	Nicotine	T. V. B. minus Nicotine as NH <sub>3</sub>	Ratio, Nicotine as NH <sub>3</sub> to T. V. B. as NH <sub>3</sub>	Ammoniacal	True NH <sub>3</sub>	T. V. A. <sup>b</sup> as Acetic Acid	Formic Acid	Ratio, T. V. A. Equivalents to T. V. B. Equivalents	Ratio, Nicotine in Smoke to Nicotine in Cigaret	Ratio, Mm. Smoked to Mm. Cigaret	Av. Cc. Smoke per Cigaret
Bright	4.91	1.65	9.72	0.63	0.62	0.40	0.19	7.13	1.17	1.23	0.23	47/70	359
Burley	8.49	2.75	13.72	1.30	0.53	0.71	0.37	6.58	0.72	0.69	0.22	47/70	283
Turkish	4.99	1.47	5.55	0.89	0.40	0.44	0.27	5.50	0.76	1.08	0.24	44/67	369
Blend	5.14	1.61	8.66	0.70	0.57	0.35	0.24	6.47	0.95	1.14	0.22	47/70	370

<sup>a</sup> Total volatile bases. <sup>b</sup> Total volatile acids.

TABLE VI. EFFECT OF PHYSICAL PROPERTIES OF CIGARETS ON THE COMPOSITION OF SMOKE (IN MG. PER LITER OF SMOKE)

Cigaret No.	Weight Grams	Circumference Mm.	Air Flow <sup>a</sup> Cc./sec.	T. V. B. <sup>b</sup> as NH <sub>3</sub>	Nicotine	T. V. B. minus Nicotine as NH <sub>3</sub>	Ratio, Nicotine as NH <sub>3</sub> to T. V. B. as NH <sub>3</sub>	T. V. A. <sup>c</sup> as Acetic Acid	Ratio, T. V. A. Equivalents to T. V. B. Equivalents	Ratio, Nicotine in Smoke to Nicotine in Cigaret
1	1.09	26.0	21.0	1.55	9.32	0.57	0.63	6.86	1.26	0.21
2	1.09	26.7	25.0	1.73	10.39	0.64	0.63	7.08	1.16	0.22
3	1.16	27.0	25.0	1.68	10.28	0.60	0.64	7.29	1.23	0.23
4	1.03	26.0	25.0	1.81	10.20	0.74	0.59	7.37	1.16	0.23

<sup>a</sup> At 3-inch (7.6-cm.) water vacuum. <sup>b</sup> Total volatile bases. <sup>c</sup> Total volatile acids.

### Physical Properties

In Table VI the effect of varying some of the physical properties of the cigaret, using the same blend of tobaccos, is shown. The changes are apparently due to differences in the area of cross section of the cigaret and to the proportion of air spaces to tobacco shreds within this area, which alter the depth of the combustion zone and the filtering action of the unburned portion of the cigaret. These factors are interdependent to such an extent that the isolation of the individual effects is difficult. The second cigaret in Table VI is normal for the particular blend studied. In the first, the area of cross section has been decreased about 8 per cent, which, when the weight is unchanged, greatly reduces the air spaces in the cigaret and increases the filtering action. The reduction in nicotine and ammonia content is about equal but greater than the acid reduction, resulting in a shift to the acid side. When the air space remains constant but the tobacco is increased as in cigaret 3, the burning zone increases in cross section but becomes shallower. Base formation is slightly inhibited, particularly in the ammonia fraction, with a resultant increase in acidity. The larger volume of smoke, however, permits a somewhat greater recovery of nicotine from the tobacco. Cigaret 4 is made somewhat smaller and the tobacco is reduced correspondingly to preserve the air flow. A deeper combustion zone accounts for the higher nicotine recovery and the greater degree of oxidation accounts for the increased ammonia content, while preserving at the same time the essential acid-base relation. It is evident that acid formation is much less affected by the physical properties than base production; consequently the determination and selection of the proper base relations and their maintenance are of prime importance in cigaret manufacture.

### Side Stream

The side-stream smoke is collected by scrubbing alternately through alcoholic and aqueous hydrochloric acid and sodium hydroxide and distilled. Although the method is still tentative, it has furnished some important information of a general character. Because of the high degree of oxidation, as compared with the main stream, the combustion products show greater degradation, tending toward simpler compounds. The smoke is decidedly alkaline with a preponderance of ammonia. Nicotine is present in quantities, although there is evidence of decomposition products of similar chemical properties in significant amounts. Under the smoking condi-

ditions described, the main-stream bases are less than 10 per cent of the side stream, while the nicotine distribution is about four to seven.

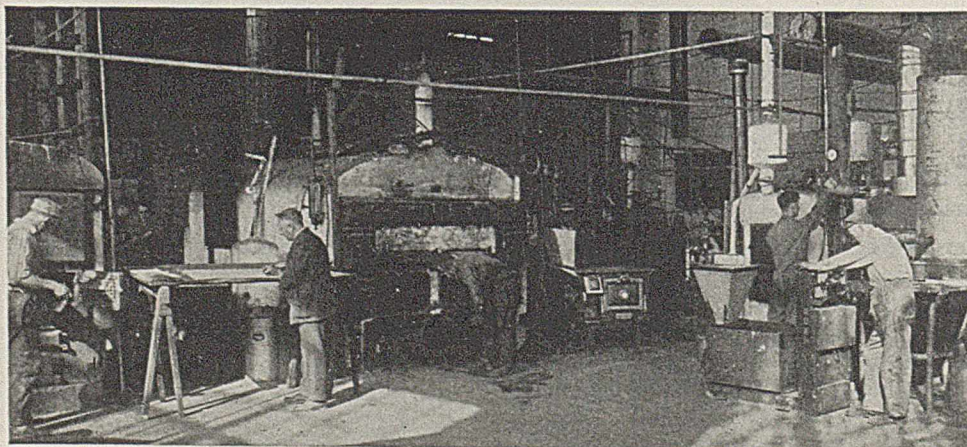
Analyses of the butts show that an appreciable amount of main-stream constituents is filtered out in the unburned portion. The increase in nicotine content of the butts is not large, but amounts to 12-15 per cent of the nicotine found in the main stream. In an exceptionally heavy and tight cigaret, it may be as high as 35 per cent.

When the various fractions of nicotine are combined after reducing to a common basis, it is found that only a limited portion is destroyed. In the popular domestic blends, from 62 to 65 per cent of the nicotine in the burned portion of the cigaret may be recovered from the main and side streams and butts. In cigarets manufactured from other tobaccos, in which the burning quality is markedly altered, the nicotine recovery may approach 80 per cent.

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RECEIVED August 20, 1936.



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# Plate Efficiency and Entrainment in Distillation

An experimental method for the separate determination of the entrainment and the Murphree and entrainment efficiencies in a distilling column is described. With mixtures of ethanol and water and of benzene and toluene the Murphree efficiency is independent of the concentration of the liquid on the plate. With benzene and toluene the entrainment is less with liquids containing 60 to 70 molar per cent of benzene than with mixtures richer or poorer in benzene. Dilute mixtures of alcohol in water give high entrainments; above 30 per cent alcohol, the entrainment is small.

THE over-all fractionating efficiency of a single plate in a distilling column may be defined as the ratio of the actual change in the composition of the liquid between plate  $n$  and plate  $n + 1$  to the change that should occur if there were perfect equilibrium between the rising vapor and the liquid on the plate and if the rising vapor carried no entrained liquid. In general, neither of these ideal conditions is realized in practice. The over-all fractionating efficiency of any actual plate is the resultant of two factors: the intimacy of contact between the rising vapor and the liquid on the plate and the amount of entrained liquid in the vapor rising to the plate. The intimacy of contact between the liquid and the vapor determines the Murphree efficiency,  $k$ —i. e., the ratio of the actual change in composition of the vapor passing through the plate to the change that should occur if there were perfect equilibrium between the liquid and the vapor. The amount of entrainment determines  $k'$ , the entrainment efficiency, which may be defined as the ratio of the actual change in composition of the liquid between plate  $n$  and plate  $n + 1$  to the change that should occur if there were no entrainment. In a column operating under such conditions that the liquid on each plate is well mixed and of uniform

## in Distillation

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composition, the over-all efficiency of the first (bottom) plate is the product of the Murphree efficiency and the entrainment efficiency, the net efficiencies of the higher plates are more complex functions of these two factors.<sup>1</sup>

The Murphree efficiency of a plate operating under otherwise constant conditions should be independent of the reflux ratio, at least within wide limits. On the other hand, the entrainment efficiency varies regularly with the reflux ratio, in accordance with the equation:

$$k' = R/[R + E(R + 1)] \quad (1)$$

where  $k'$  = entrainment efficiency  
 $R$  = reflux ratio, molar ratio of reflux to withdrawn product  
 $E$  = entrainment, moles of liquid entrained in 1 mole of rising vapor

If we make two batch distillations, under otherwise similar conditions, with reflux ratios of  $R_1$  and  $R_2$ , respectively, and measure the corresponding over-all efficiencies,  $A_1$  and  $A_2$ , of the bottom plate of the column, we have the following relations:

$$A_1 = kR_1/[R_1 + E(R_1 + 1)] \quad (2)$$

$$A_2 = kR_2/[R_2 + E(R_2 + 1)] \quad (3)$$

If we let  $A = A_1/A_2$  and if one of the experimental distillations is made with an infinite reflux ratio ( $R_1 = \infty$ ) and the other with a reflux ratio of 1:1 ( $R_2 = 1$ ), we have:

$$E = (A - 1)/(2 - A) \quad (4)$$

Thus, by making two experimental batch distillations at reflux ratios of infinity and unity, respectively, under otherwise identical conditions, and measuring the over-all fractionating efficiency of the lowest plate in each distillation, we can compute the amount of entrainment. The entrainment efficiency in the distillation made with an infinite reflux ratio is

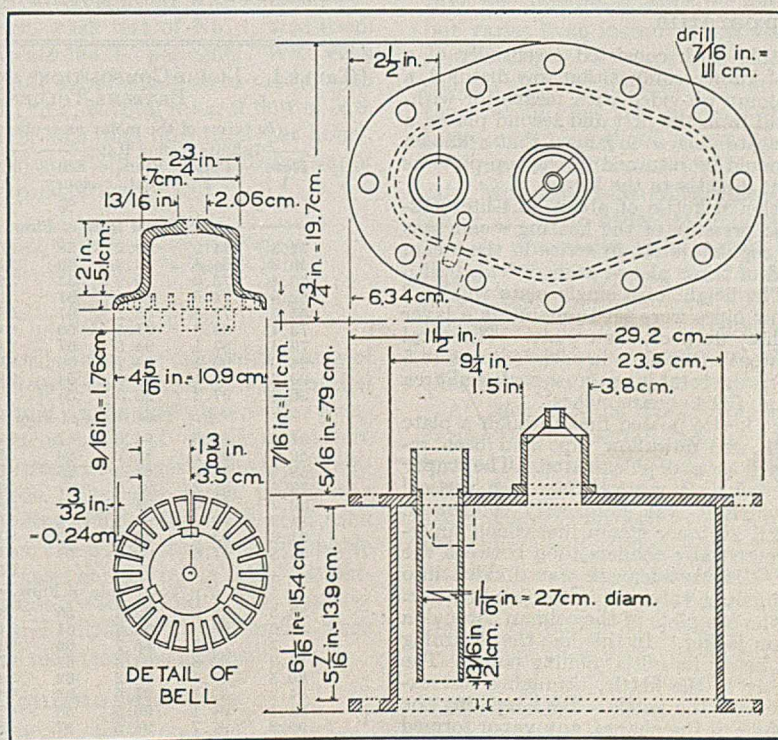


FIGURE 1. DETAILS OF COLUMN SECTION AND BELL

<sup>1</sup> Rhodes, F. H., IND. ENG. CHEM., 26, 1333 (1934); 27, 272 (1935).

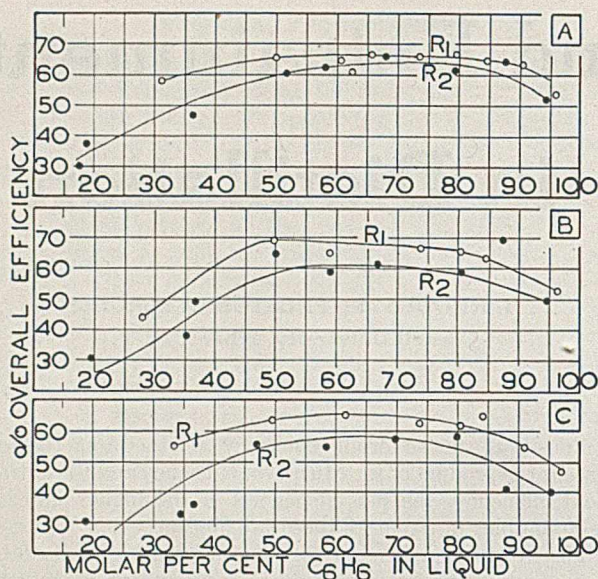


FIGURE 2. VARIATION OF OVER-ALL EFFICIENCY WITH MOLAR FRACTION OF BENZENE

A = 5 gallons, B = 8 gallons, C = 9.6 gallons per hour  
 $R_1$  = infinite reflux ratio,  $R_2$  = reflux ratio of 1 to 1

$1/(1 + E)$ ; that in the distillation made with a reflux ratio of unity is  $1/(1 + 2E)$ . The Murphree efficiency in each distillation can be computed from the general relations:

$$A_1 = kk'_1, \text{ and } A_2 = kk'_2$$

In any actual case, both the entrainment efficiency and the Murphree efficiency will vary with the design of the plate, the distance between plates in the column, and the rate of flow of vapor through the column. It is also possible that the separate efficiency factors may depend upon the nature and the relative amounts of the components on the liquid mixture on the plate. In this investigation we have measured the change in entrainment efficiency with change in composition of mixtures of ethanol and water and of benzene and toluene.

### Apparatus

The apparatus used in this work consisted essentially of a kettle in which a mixture of known composition was distilled, a three-plate fractionating column provided with means for withdrawing samples of the liquid from the first and second plates, a total condenser, and condensate lines so arranged that a known fraction of the condensate could be returned to the top plate as reflux while the rest was sent directly to the kettle.

The still was a steam-jacketed kettle of about 45.4-liter (12-gallon) total capacity. The pressure of the heating steam was controlled by two pressure regulators set in series in the steam line. The column consisted of three plates, each provided with a single bell (Figure 1). The height of a single plate was 15.2 cm. (6 inches); the downflow pipes were set to maintain a layer of liquid 3.2 cm. (1.25 inches) deep on each plate. The total cross-sectional area of the twenty-four slots in each bell was 14.5 sq. cm. (2.25 square inches); the total inner cross-sectional area of the column was 210 sq. cm. (32.4 square inches).

The vapor rising from the kettle passed first through a plate section from which the bell and downflow pipe had been removed. This section served as a dephlegmator. The vapor from the top plate was carried by a vertical riser to a vertical water-tube condenser in which it was completely condensed. This riser was provided with an inner steam line which superheated the vapor and prevented any condensation between the column and the condenser. The condensate was divided into reflux and product by a regulating valve set in the product line. The reflux was returned to the top plate of the column through a U-line provided with a steam jacket. In this line the returning reflux was reheated to just below its initial boiling point. The product was returned directly to the kettle, through a line extending almost to the bottom of the kettle. By admitting the product deep below the surface of the charge, any vapor formed by the flashing of the low-boiling returned product was passed through the main part of the charge and brought into equilibrium

with it. Both reflux line and product line were provided with weirs for measuring the rate of flow.

The kettle was equipped with an outlet, through a cooler, through which a sample of the charge could be withdrawn for analysis. The product was sampled through a pet cock just below the measuring weir. Through ports drilled at an angle through the sides of the column, samples of the liquid leaving plate 1 and of the liquid leaving plate 2 were withdrawn through ice-cooled lines. The entire apparatus was well insulated.

### Procedure

The kettle was charged with about 15 liters (4 gallons) of the material to be distilled, heating steam was admitted to the jacket, and the pressure regulators were set to give the desired total rate of distillation. The valve in the product line was adjusted to maintain the desired reflux ratio; sufficient steam was admitted to the preheater in the reflux line to keep the reflux at about  $2^\circ\text{C}$ . below its initial boiling point. After equilibrium conditions had been maintained for one hour, samples (125 cc.) of the charge in the kettle, the product, the liquid from plate 1, and the liquid from plate 2 were slowly withdrawn.

The compositions of mixtures of ethanol and water were computed from the densities, as determined at  $20^\circ\text{C}$ . by a specific gravity bob. The reported molar fractions of ethanol are probably accurate within 0.1 per cent. The mixtures of benzene and toluene were analyzed by an empirical distillation method. The sample to be analyzed was dried over fresh granular anhydrous calcium chloride for at least 12 hours. A 100-cc. sample of the dry mixture was then distilled from a special 200-cc. distilling flask (Corning Glass Works No. 1610) at the rate of exactly two drops per second. The temperature of the vapor was indicated by a calibrated thermometer ( $+70^\circ$  to  $+160^\circ\text{C}$ . in  $0.2^\circ$  divisions,  $9^\circ$  per inch) set so that the top of the auxiliary bulb of the thermometer was level with the middle of the opening into the outlet tube of the distilling flask. The vapor was condensed in a glass condenser tube 1.27 cm. (0.5 inch) in internal diameter and 61 cm. (24 inches) long, set at an angle of  $20^\circ$  from the horizontal and cooled with ice and water. The distilling flask was supported on a square of asbestos board provided with a circular hole 2.5 cm. (1 inch) in diameter. The distillate was

TABLE I. LIQUID COMPOSITIONS AND OVER-ALL EFFICIENCIES OF BENZENE-TOLUENE MIXTURES

(In terms of the molar percentage of benzene in the liquid)							
Infinite Reflux Ratio				Reflux Ratio, 1 to 1			
Plate 1	Plate 2	Product	Efficiency %	Plate 1	Plate 2	Product	Efficiency %
A. Total Rate of Flow = 5 Gallons/Hour							
31.3	44.2	69.2	58	17.8	20.8	43.5	30
49.8	64.5	83.4	66	19.0	23.1	46.3	38
60.4	73.0	85.9	65	36.4	42.2	68.7	37
62.6	74.0	86.4	61	51.7	60.4	81.3	60
65.5	77.3	88.2	67	58.0	66.5	85.0	63
73.4	83.0	91.5	66	68.1	75.5	89.0	66
79.4	87.1	94.5	67	79.7	85.2	93.6	62
84.2	90.1	94.7	65	87.5	91.7	95.9	65
90.3	94.1	96.0	64	94.5	96.1	98.0	52
96.0	97.3	98.3	54				
B. Total Rate of Flow = 8 Gallons/Hour							
28.6	38.5	64.6	47	19.5	22.9	46.3	31
50.3	65.7	81.7	69	35.2	40.8	67.3	38
58.8	71.7	85.2	65	37.0	43.8	70.2	49
73.6	83.2	91.0	67	50.0	59.8	80.2	65
80.2	87.6	94.3	66	59.0	67.2	85.0	59
84.2	90.0	94.7	64	67.0	76.2	89.0	62
91.2	93.9	96.5	50	80.3	85.6	93.6	59
96.8	97.8	98.5	53	87.5	92.0	96.0	70
				94.8	96.2	98.4	50
C. Total Rate of Flow = 9.6 Gallons/Hour							
33.5	46.2	72.2	56	18.7	22.0	44.8	31
48.9	63.3	82.8	64	34.4	39.6	65.2	33
61.3	74.1	86.7	66	36.6	42.1	67.1	36
73.8	82.8	93.3	63	47.0	55.1	78.3	56
80.5	87.3	94.2	62	58.6	66.3	84.6	55
84.2	90.1	94.6	65	70.0	76.8	89.0	58
91.1	94.1	96.5	55	80.2	85.5	93.6	59
96.8	97.7	98.5	47	88.2	90.8	96.0	41
				95.0	96.2	98.1	40

collected in a graduated cylinder. The exact temperatures at which 5, 10, 25, 50, 75, 90, and 95 cc. of distillate were collected were observed. To the observed temperatures corrections were applied to compensate for the difference between the actual barometric pressure and 760 mm. For temperatures between 80° and 90° C., this correction was 0.043° C. for each mm. difference in pressure; for temperatures between 90° and 100° C. the correction was 0.045° C. per mm.; for temperatures between 100° and 110° C. the correction was 0.047° C. per mm.

A series of such test distillations was made with synthetic mixtures of known percentages of benzene and toluene. From these results graphs were drawn, each graph representing the variation in the corrected temperature, at one fixed percentage, with the change in the molar fraction of benzene in the sample. By comparison with these standard graphs, the results of the test distillation of mixtures of unknown composition were interpreted.

With mixtures containing more than 85 or less than 15 per cent of benzene, the difference between the temperature at which 10 per cent of the mixture distills and that at which 90 per cent distills changes rapidly with the composition. For such mixtures graphs were drawn in which the difference between the 10 and the 90 per cent points was shown as a function of the molar fraction of benzene in the sample. These graphs were used in the analysis of samples containing relatively small or relatively large amounts of benzene.

This distillation method of analysis is probably accurate within about 1 per cent, even in the case of mixtures containing about equal amounts of the two components. For mixtures containing relatively small or relatively large amounts of benzene the method is probably accurate within about 0.2 per cent.

## Results

Experiments were made with mixtures of benzene and toluene and of ethanol and water. Nitration grade pure benzene, produced by the refining of material from coke-oven light oil, was used. It showed a distillation range of 0.6° C., a melting point of 5.25° C., and an acid-wash test of No. 1. Nitration grade pure toluene from coke-oven light oil, with a distillation range of 0.4° C. and an acid-wash test of No. 1, was used. The ethanol was pure grain alcohol, 95 per cent. With each pair of liquids, three series of experiments were made, with reflux ratios of infinity and 1 to 1, at total rates of flow of 5, 8, and 9.6 gallons per hour (19, 30.3, and 36.3 liters per hour). These rates correspond approximately to the following vapor velocities through the free space of the tower:

Rate		Vapor Velocity			
Gal./hr.	L./hr.	Ethanol-Water		Benzene-Toluene	
		Ft./sec.	M./sec.	Ft./sec.	M./sec.
5	19	0.6	0.18	0.26	0.08
8	30.3	0.96	0.29	0.42	0.13
9.6	36.3	1.15	0.35	0.51	0.155

In each of the series of distillations, the relative amounts of the components were varied to give a considerable variation in the composition of the liquid on the first plate. The over-all efficiencies measured in each set of experiments were plotted as ordinates against the percentages of the more volatile component as abscissas. Through these points the smooth curves best representing the results obtained at each reflux ratio were drawn; from these graphs the most probable values for the over-all efficiencies at each reflux ratio, for mixtures of identical composition, were found. The entrainments and the Murphree and entrainment efficiencies were computed from the values as read from the graphs.

### Benzene-Toluene Mixtures

The values for the over-all efficiencies for mixtures of benzene and toluene are shown in Table I and Figure 2. At

TABLE II. ENTRAINMENTS AND EFFICIENCIES IN DISTILLATION OF BENZENE-TOLUENE MIXTURES

X	A <sub>1</sub>	A <sub>2</sub>	A	E	k' <sub>1</sub>	k' <sub>2</sub>	k
Total Rate of Flow = 5 Gallons/Hour							
30	0.57	0.46	1.24	0.31	0.76	0.62	0.75
40	0.62	0.54	1.15	0.18	0.85	0.73	0.73
50	0.66	0.60	1.10	0.11	0.90	0.82	0.73
60	0.67	0.63	1.065	0.07	0.93	0.88	0.77
70	0.67	0.65	1.03	0.03	0.97	0.94	0.69
80	0.66	0.64	1.03	0.03	0.97	0.94	0.68
90	0.64	0.58	1.10	0.11	0.90	0.82	0.71
Average (30-90%)							0.72 ± 0.03
Total Rate of Flow = 8 Gallons/Hour							
30	0.47	0.36	1.3	0.43	0.70	0.54	0.67
40	0.60	0.50	1.2	0.25	0.80	0.67	0.75
50	0.69	0.59	1.17	0.20	0.83	0.71	0.83
60	0.68	0.61	1.115	0.13	0.88	0.79	0.77
70	0.67	0.61	1.10	0.11	0.90	0.82	0.75
80	0.66	0.59	1.12	0.14	0.87	0.78	0.76
90	0.59	0.53	1.11	0.13	0.88	0.79	0.67
Average (30-90%)							0.74 ± 0.04
Total Rate of Flow = 9.6 Gallons/Hour							
30	0.53	0.38	1.4	0.67	0.60	0.43	0.87
40	0.60	0.50	1.2	0.25	0.80	0.67	0.75
50	0.65	0.56	1.14	0.13	0.87	0.79	0.74
60	0.66	0.58	1.14	0.13	0.87	0.79	0.76
70	0.65	0.58	1.12	0.127	0.89	0.80	0.73
80	0.62	0.54	1.15	0.135	0.88	0.79	0.70
90	0.56	0.45	1.25	0.33	0.75	0.60	0.75
Average (30-90%)							0.77 ± 0.04

each rate of distillation the over-all efficiency increases with increase in the concentration of benzene until a maximum is reached at about 70 molar per cent benzene, and then decreases. The experimental error in the determination of the over-all efficiency is greater with mixtures containing relatively large or relatively small percentages of benzene, since in such mixtures the vapor composition curve of the McCabe and Thiele diagram lies near the enrichment line, and even slight errors in analysis may result in considerable errors in the computed efficiencies. In the determination of the plate efficiencies with mixtures low in benzene, another source of error is involved; most of the benzene in the system is concentrated in the relatively small amount of material on the plates and in the flow lines, so that the withdrawing of even small samples may disturb the equilibrium in the system. Furthermore, particularly at high rates of flow, it is probable that the amount of entrainment is not absolutely constant but varies from instant to instant, so that somewhat erratic results are to be expected. Despite all of these possible sources of error, the data appear to indicate consistently that the over-all efficiency passes through a maximum with mixtures containing about 70 per cent benzene.

The computed values for the entrainment and for the separate Murphree and entrainment efficiencies are shown by Table II. The Murphree efficiency at each rate of distillation is practically independent of the composition of the liquid. There appears to be a slight but consistent increase in the Murphree efficiency with increase in the rate of distillation. This may be attributed to the somewhat increased splashing and spray formation, with resulting increase in the effectiveness of contact between liquid and vapor.

At each rate of distillation the amount of entrainment varies with the composition of the liquid. With low percentages of benzene the entrainment is high; with increasing concentration of benzene the entrainment decreases and then again slightly increases. An increase in the rate of distillation from 5 to 8 gallons per hour results in a distinct and general increase in the entrainment; further increase of the rate to 9.6 gallons per hour has little further effect except with liquids containing 30 to 90 per cent of benzene.

Through glass windows set in the sides of the top plate, the behavior of the liquid could be observed. With the mixtures of benzene and toluene there was no foaming, but there were vigorous splashing and some considerable spray formation. There was little apparent difference in behavior with change

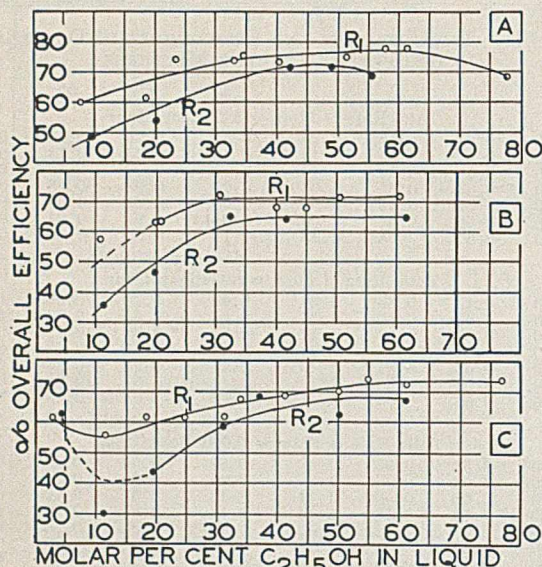


FIGURE 3. VARIATION OF OVER-ALL EFFICIENCY WITH MOLAR FRACTION OF ETHANOL

A = 5 gallons, B = 8 gallons, C = 9.6 gallons per hour  
 $R_1$  = infinite reflux ratio,  $R_2$  = reflux ratio of 1 to 1

in concentration, although the spray obtained with liquids very rich or very poor in benzene appeared to consist of smaller drops. Apparently the variation in entrainment with composition was due to variation in drop size rather than to any very marked change in the manner of boiling.

### Ethanol-Water Mixtures

Table III and Figure 3 show the results with ethanol and water. All data obtained with mixtures containing less than 20 per cent alcohol are probably inaccurate. With low concentrations of alcohol on the plate, so little of this component remained in the kettle that the withdrawing of the samples changed the conditions in the system markedly. Furthermore, the forms of the McCabe and Thiele diagram are such

TABLE III. LIQUID COMPOSITIONS AND OVER-ALL EFFICIENCIES OF ETHANOL-WATER MIXTURES

(In terms of the molar percentage of ethanol in the liquid)							
Infinite Reflux Ratio				Reflux Ratio, 1 to 1			
Plate 1	Plate 2	Product	Efficiency %	Plate 1	Plate 2	Product	Efficiency %
A. Total Rate of Flow = 5 Gallons/Hour							
7.7	27.2	58.7	60	9.6	20.0	56.7	49
18.5	39.3	64.1	62	20.1	32.3	63.5	54
23.2	46.6	65.9	75	42.3	51.9	67.4	72
33.2	52.1	68.7	74	48.9	56.8	69.9	72
34.5	52.7	68.9	75	55.3	60.8	71.6	69
40.6	56.1	70.1	74				
51.3	62.3	72.7	75				
57.1	65.8		78				
61.5	68.5	76.0	78				
77.7	79.7	82.4	69				
B. Total Rate of Flow = 8 Gallons/Hour							
11.0	31.1	50.5	58	11.5	42.2	52.0	36
20.1	40.8	63.5	63	20.0	31.4	61.3	47
20.5	40.7	66.2	62	32.5	45.0	64.8	65
30.3	49.9	67.7	72	41.5	52.2	65.8	64
39.9	54.2	69.0	67	61.3	63.0	76.3	65
51.3	61.6	68.2	71				
60.3	67.0	75.2	71				
C. Total Rate of Flow = 9.6 Gallons/Hour							
3.1	16.1	52.0	62	4.7	10.4	49.2	63
11.3	30.7	60.3	56	11.2	20.4	50.3	30
18.5	39.3	64.7	62	19.4	30.8	60.0	44
24.6	43.5	64.1	62	31.2	43.2	64.2	60
31.3	47.7	66.3	62	37.3	49.0	66.3	69
33.9	50.8	67.8	68	50.3	57.3	69.5	63
41.2	55.5	69.3	69	61.2	63.0	76.1	67
50.1	61.0	72.5	71				
55.1	64.3		75				
61.6	68.0	75.2	73				
76.8	79.1	82.0	74				

that, with mixtures containing less than about 20 or more than about 60 per cent ethanol, even slight errors in analysis or sampling or slight variations in conditions may result in large errors in the computed efficiencies.

In general, the over-all efficiencies are low with low concentrations of alcohol and rise rather rapidly as the concentration increases to 30 per cent. Further increase in concentration has comparatively little effect.

The entrainments and the separate efficiency factors are shown in Table IV. The Murphree efficiency appears to be about constant at approximately 80 per cent, irrespective of the concentration. Entrainment is high with mixtures containing less than 30 per cent alcohol; with liquids rich in alcohol there is little entrainment. With low concentrations the entrainment increases rapidly with increase in the rate of distillation; with high concentrations the apparent variation is within the possible limit of error of the experiment.

TABLE IV. ENTRAINMENTS AND EFFICIENCIES IN DISTILLATION OF ETHANOL-WATER MIXTURES

X	$A_1$	$A_2$	A	E	$k'_1$	$k'_2$	k
Total Rate of Flow = 5 Gallons/Hour							
10	0.62	0.49	1.26	0.35	0.74	0.59	0.84
20	0.67	0.58	1.16	0.19	0.84	0.72	0.80
30	0.72	0.65	1.11	0.12	0.89	0.80	0.81
40	0.76	0.71	1.07	0.07	0.93	0.87	0.82
50	0.77	0.72	1.07	0.07	0.93	0.87	0.83
Average (10-50%)							0.82 ± 0.02
Total Rate of Flow = 8 Gallons/Hour							
10	0.50	0.33	1.51	1.04	0.495	0.325	1.00 (?)
20	0.63	0.50	1.26	0.35	0.74	0.59	0.85
30	0.70	0.62	1.13	0.15	0.87	0.77	0.80
40	0.71	0.65	1.09	0.11	0.90	0.82	0.79
50	0.72	0.65	1.11	0.12	0.89	0.80	0.81
60	0.72	0.65	1.11	0.12	0.89	0.80	0.81
Average (20-60%)							0.81 ± 0.02
Total Rate of Flow = 9.6 Gallons/Hour							
5	0.58	0.58	1.00	0	1	1	0.58 (?)
10	0.55	0.42	1.3	0.47	0.67	0.52	0.82
20	0.60	0.45	1.33	0.5	0.67	0.50	0.90
30	0.65	0.58	1.12	0.14	0.88	0.79	0.74
40	0.69	0.65	1.06	0.06	0.95	0.88	0.73
50	0.73	0.68	1.07	0.07	0.94	0.87	0.78
60	0.74	0.68	1.09	0.10	0.91	0.83	0.81
Average (10-60%)							0.78 ± 0.05

With mixtures of alcohol and water the change in the concentration of ethanol results in a marked change in the manner of boiling. When the concentration is high, the liquid on the plate splashes, but there is comparatively little formation of fine spray and no foaming. With rather low concentrations, froth forms on the liquid, sometimes to such an extent that the foam fills the section and is carried to the next higher plate. The low over-all efficiencies and large entrainments observed with the liquids low in alcohol are due to this foaming. With liquids that are very low in alcohol, this foaming again disappears. In a few distillations made with very dilute mixtures the values for the over-all efficiencies were comparable with those obtained with mixtures rich in alcohol. Because of the possibility of rather large experimental errors in these experiments, the quantitative results are not given here.

There is no evident reason for the observed existence of a "critical foaming range" of relatively low concentrations of ethanol in water. Neither the surface tension nor any other of the physical properties of the solutions appears to show any abnormalities within this region. The pure grain alcohol used satisfied the usual analytical requirements for such material. It is possible that small amounts of foreign substances in the original material or small amounts of impurities formed by the oxidation or other chemical change of the alcohol during the distillation may be responsible for the foaming.

### Conclusions

Both with mixtures of ethanol and water and of benzene and toluene the Murphree efficiency is independent of the

relative amounts of the components in the mixture. In the case of mixtures of alcohol and water, the Murphree efficiency appears to be substantially independent of the rate of distillation; with mixtures of benzene and toluene the increased splashing incident to increase in the rate of flow appears to cause a slight increase in the Murphree efficiency.

With mixtures of benzene and toluene the liquids containing about 60 to 70 per cent benzene show the maximum over-all efficiencies. When the percentage of benzene is very high or very low, the entrainment increases and the over-all efficiency decreases. With aqueous alcohol the entrainment is relatively high when the concentration of alcohol is low; increase of the alcohol content above about 30 per cent results in little further change in the amount of entrainment or in the over-all efficiency.

In the intelligent design of a distilling column for any specific purpose, due attention should be paid to the component factors that determine the over-all fractionating efficiencies of the plates and to the variation of these separate factors with

the composition of the liquid, the rate of flow of the vapor, and other conditions. For example, these results indicate that, in the design of an alcohol still, entrainment may be particularly serious on those plates carrying low concentrations of alcohol and that such plates should be widely spaced and designed to operate with low vapor velocities, whereas the upper plates of the column may be more closely spaced and operated at higher vapor velocities.

Attempts to measure the amount of entrainment in a column by blowing air or gas through water or oil on the plates and to apply the data thus obtained to the prediction of the performance of the column under actual operating conditions are probably of little value. The entrainment varies so widely with the nature and concentration of the liquid that significant results can be obtained only by measurements made under conditions that approach, as closely as possible, those under which the column is to operate.

RECEIVED July 2, 1936.

# Effect of Salts on Detergent Action of Soap

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**T**HE detergent power of a specific soap solution varies with the alkalinity (6, 7), and the addition of an alkaline builder at first increases and then decreases the detergent efficiency (4). With sodium hydroxide, sodium carbonate, and trisodium phosphate the maximum effectiveness is exhibited when the solution has a pH of about 10.73 at room temperature (4). The maximum detergent power obtained, at optimum alkalinity, with solutions of the same concentration of the same soap varies considerably with the nature of the added builder. These results indicate that the effect of the builder is not due solely to its action in altering the alkalinity of the solution but is to be attributed, in part at least, to the specific effects of the added anions or cations, or both. In this investigation an attempt was made to determine the specific effects of certain anions on the detergent power of soap at the optimum alkalinity.

## Experimental Methods

The effectiveness of the added builder was measured as follows:

Samples of cotton cloth were soiled to a standard darkness by a standard soiling solution, and were then subjected to four successive washings with a washing solution of standard alkalinity and soap concentration and of known concentration of builder. The whiteness of the final sample was measured. The effect of the builder was expressed in terms of the percentage ratio of the increase in brightness in four washes with the soap solution containing the builder, to the increase in brightness in four washes with soap solution, without builder, of the same concentration and alkalinity.

In washing tests made with artificially soiled cloth at 60° C., the detergent action of a 0.25 per cent soap solution is at a maximum when the alkalinity of the solution is adjusted to a pH of about 9.66. The addition of sodium chloride, sulfate, or phosphate to soap solutions at the optimum pH at first increases and then decreases the detergent effect. The effectiveness of the added salt at the optimum concentration is approximately proportional to the valence of the anion of the added salt. Sodium borate and acetate do not enhance the detergent action of the soap.

The laboratory washing machine was similar to that described by Rhodes and Brainard (5). The soiling solution was prepared by grinding together 2 parts by weight of carbon black (Dar brand, Standard Carbon Company), 3 parts of Crisco, and 5 parts of medium-viscosity paraffin-base petroleum lubricating oil, and diluting 10 grams of the resulting paste with 2 liters of carbon tetrachloride. The cloth used was Utica cotton sheeting (68 to 70 thread count), freed from starch and filler by treatment with diastase solution, followed by thorough washing with soap solution, rinsing, drying, and ironing. The ironed cloth took the soil much more evenly than did unironed cloth. A strip of the cleaned cloth 14 cm. wide and 100 cm. long was passed three times through 200 cc. of the soiling solution in a shallow dish. After each pass the cloth was allowed to dry in the air. After the last pass the cloth was dried for an hour at 80° C. and was then aged for 11 hours at room temperature before washing. The prepared cloth was made into bags 10 cm. square, and the brightness was measured. Into each bag were placed 100 grams

of 5-mm. glass beads, and two of the filled bags were washed simultaneously in the machine. The washing temperature was 60° C., the time for each wash was 7.5 minutes, the speed of the machine was 80 r. p. m., and the volume of washing solution was 500 cc. The washed bags were rinsed by dipping five times in each of the following solutions: (a) detergent solution of the same composition as that used in washing, (b) and (c) distilled water, (d) 0.05 N acetic acid, and (e) distilled water. The beads were removed, the bags were pressed flat between filter paper and dried at 80° C., and the brightness was measured.

A reflectometer similar to that described by Rhodes and Brainard (5) was used to measure the brightness. Instead of using a photometer of the Lummer-Brodhun type for measuring the intensity of the reflected light, a photoelectric tube (General Electric No. PJ-22) was employed. The tube was connected

with a 45-volt B battery and a swinging coil galvanometer (Leeds & Northrup No. 2500F) with a sensitivity of 0.0001 microampere per mm. scale division at one meter. The lighting tube for the reflectometer was provided with a 50-candle-power incandescent bulb, backed by a chromium-plated reflector and carrying  $4.70 \pm 0.02$  amperes from a storage battery circuit. The light was rendered parallel by an achromatic doublet lens. A water-cooled copper tube was wrapped around the end of the lighting tube to prevent overheating from the bulb.

This reflectometer was calibrated by comparison with a reflectometer provided with a photometer of the Lummer-Brodhun type. Samples of cloth ranging in brightness from about 75 to 25 per cent were measured on both instruments; from the results, a calibration curve was drawn that permitted the translation of the readings from the light-sensitive cell into terms of true brightness. The calibration was checked at frequent intervals.

The standard soap used in these experiments was a commercial white soap flake of the following analytical characteristics:

Moisture, %	1.5	Glycerol, %	0.40
Free alkali	0.00	Total alkali (as $\text{Na}_2\text{O}$ ), %	10.91
Free fatty acid	0.00	Titer of fatty acids, °C.	34.3
Sodium chloride, %	0.82		

Other chemical materials were of standard c. p. grade unless otherwise specified.

### Measurement of pH of Soap Solutions

The alkalinities of the various detergent solutions used in these experiments were computed from the results of measurements of the electromotive force developed between a hydrogen electrode immersed in the solution and a standard 0.1 *N* calomel electrode.<sup>1</sup> The measurements were made by the general method described by McBain and Martin (2). The temperature of the washing solution containing the hydrogen electrode was 60° C. The solution was connected by a salt bridge of saturated potassium chloride (also at 60° C.) with a calomel electrode at room temperature. The mercury used in the calomel electrode was prepared by the electrolysis of a solution of purified mercuric perchlorate, following the procedure described by Newbery (3). The mercurous chloride was prepared by dissolving some of the pure metal in redistilled nitric acid, precipitating the chloride with purified and redistilled hydrochloric acid, and washing the precipitate thoroughly with distilled water. The hydrogen electrode consisted of a sheet of platinized platinum, supplied with purified hydrogen. The hydrogen was humidified by passage through water at 60° C. before being admitted to the electrode. The usual corrections were applied to correct for the deviations from standard atmospheric pressure, for the partial pressure of the water vapor in the hydrogen, and for the difference in temperature between the hydrogen electrode and the calomel electrode. With the apparatus used, a value of 0.7798 volt was obtained for the difference between the electromotive force of the calomel electrode and the hydrogen electrode immersed in 0.1 *N* sodium hydroxide at 90° C. This value agrees well with that of 0.7797 reported by McBain and Martin (2). Solutions prepared by mixing

<sup>1</sup> The measured difference in electromotive force was corrected for the deviation of the pressure of the hydrogen from the standard value of 760 mm. of mercury and for the partial pressure of the water vapor in the hydrogen. The correction was computed as follows:

$$\text{Correction (volts)} = 0.0591/2 \log 760/(B - P_w)$$

where *B* = barometric pressure, mm. Hg

*P<sub>w</sub>* = vapor pressure of water at 60° C.

The value for the electromotive force of the calomel electrode at 25° C. was taken as 0.3376 volt. The temperature coefficient was 0.00079 volt per degree, so that the electromotive force at 60° C. was computed as  $0.3376 - (60 - 25) \times 0.00079 = 0.3376 - 0.0277$  volt. The difference in potential between the hypothetical normal hydrogen electrode and the 0.1 *N* calomel electrode at 25° C. is 0.3376 volt at 25° C. and 0.3317 volt at 60° C. The change in this difference with temperature is 0.0059 volt. The corrected equation by which the pH was computed from the measured difference in potential was:

$$\text{pH} = \frac{\text{Corrected e. m. f.} - (0.3376 - 0.0277 + 0.0059)}{0.000198 (273 + 60)}$$

together equal volumes of Sorensen's standard borate buffer solution (1) and a 0.1 *N* solution of sodium hydroxide gave, for the value of the pH at 60° C., an average value (in five measurements) of 10.13, with an arithmetical mean deviation of 0.02. This compares with a published value (1) of 10.19.

The pH of a 0.25 per cent solution of the soap used in the washing experiment was 10.19 at 22° C. and 9.30 at 60° C. The value of the pH at the higher temperature is the average of five individual measurements, with a mean deviation of 0.03.

To a solution containing 0.25 per cent of the soap, different known amounts of a standardized solution of sodium hydroxide were added. The pH of each mixture at 60° C. was then determined. The results were as follows:

NaOH Equivalent Mg./l.	pH	NaOH Equivalent Mg./l.	pH
0.00	9.30	0.8	9.66
0.4	9.36	1.0	9.74
0.6	9.48	1.2	9.83

### Results of Washing Tests

Four pairs of soiled samples were washed with a 0.25 per cent soap solution, according to the procedure described. In each case the two individual samples of soiled fabric that constituted a pair were washed together through four washes. The brightness of each sample of washed, rinsed, and dried cloth was measured. At least four measurements of the brightness of each sample were made; the individual measurements were made at different points on the two sides of the bag. The following values are the averages of the several individual results obtained with each sample; the individual measurements on a single sample agreed within a maximum variation of one per cent in brightness:

Pair No.	% Increase in Brightness	
	Sample 1	Sample 2
1	21.6	21.6
2	20.5	20.4
3	21.3	20.9
4	21.6	21.9
Average <sup>a</sup>		21.2 ± 0.5

<sup>a</sup> The indicated limit of error is the arithmetical mean of the observed variations from the average value.

Samples of soiled cloth were washed with 0.25 per cent solutions of the soap containing different amounts of free sodium hydroxide. In all cases two samples of the soiled fabric were washed together through four washes, rinsed, and dried; and measurements of brightness were made at four or more points on the surface of each bag. In a few cases duplicate washing experiments were also made. The measurements on two individual bags washed together through four washes agreed within a maximum deviation of 0.6 per cent in brightness and an average deviation of  $\pm 0.3$  per cent. The results obtained when two bags were washed separately through four washes showed practically the same consistency as did the results obtained when the two bags were washed together through four washes. The following results were obtained:

NaOH Equivalent Mg./l.	pH	Increase in Brightness %	NaOH Equivalent Mg./l.	pH	Increase in Brightness %
0.00	9.30	21.2	0.8	9.66	22.45
0.4	9.36	21.0	1.0	9.74	20.55
0.6	9.48	21.6	1.2	9.83	20.0

These results agree with those of Rhodes and Bascom (4):

(1) The addition of sodium hydroxide to a soap solution at first increases and then decreases the detergent effect; (2) the optimum concentration of sodium hydroxide, with the particular soap used, is about 0.8 mg. equivalent per liter; and (3) the effect of the sodium hydroxide is not very pronounced. The present results indicate that the maximum washing effect is obtained when the pH of the soap solution



TABLE I. EFFECT OF SALTS ON WASHING EFFICIENCY

Salt Equivalent Mg./l.	pH	Increase in Brightness %	E <sup>a</sup>	pH	Increase in Brightness %	E <sup>a</sup>
—NaCl Added—						
0.0	9.66	22.45	100	9.66	22.45	100
0.5	9.66	21.5	96	9.69	21.3	95
1	9.65	22.8	102	9.69	21.5	96
2	9.65	23.3	104	9.67	22.95	102
5	9.68	23.5	105	9.72	23.3	104
10	9.68	22.8	102	9.70	23.7	107
20	9.71	18.7	83	9.64	24.3	108
50	9.69	16.8	75	9.69	20.9	93
—Na <sub>2</sub> SO <sub>4</sub> Added—						
0.0	9.66	22.45	100	9.66	22.45	100
0.5	9.66	23.55	105	9.63	20.7	92
1	9.65	24.3	108	9.62	20.8	93
2	9.67	25.0	111	9.69	21.0	94
5	9.65	25.85	115	9.67	21.2	94
10	9.66	25.75	115	9.63	21.6	95
20	9.67	20.5	91	9.66	20.4	91
50	9.68	19.1	85	9.69	19.8	88
—Na <sub>2</sub> HPO <sub>4</sub> Added—						
0.0	9.66	22.45	100	9.66	22.45	100
0.5	9.65	24.9	111	9.71	18.5	82
1	9.66	25.2	112	9.64	19.1	85
2	9.67	25.7	114.5	9.66	19.4	86
5	9.65	27.6	123	9.66	20.3	90
10	9.66	25.9	115.5	9.67	21.2	94
20	9.62	20.4	91	9.66	21.2	94
50	9.67	18.8	84	9.66	20.1	90
—Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> Added—						
0.0	9.66	22.45	100	9.66	22.45	100
0.5	9.66	23.55	105	9.63	20.7	92
1	9.65	24.3	108	9.62	20.8	93
2	9.67	25.0	111	9.69	21.0	94
5	9.65	25.85	115	9.67	21.2	94
10	9.66	25.75	115	9.63	21.6	95
20	9.67	20.5	91	9.66	20.4	91
50	9.68	19.1	85	9.69	19.8	88
—Na <sub>2</sub> H <sub>2</sub> O <sub>7</sub> Added—						
0.0	9.66	22.45	100	9.66	22.45	100
0.5	9.65	24.9	111	9.71	18.5	82
1	9.66	25.2	112	9.64	19.1	85
2	9.67	25.7	114.5	9.66	19.4	86
5	9.65	27.6	123	9.66	20.3	90
10	9.66	25.9	115.5	9.67	21.2	94
20	9.62	20.4	91	9.66	21.2	94
50	9.67	18.8	84	9.66	20.1	90

<sup>a</sup> E = ratio of increase in brightness in four washes with the salt solution to the increase in brightness in four washes with a 0.25 per cent soap solution, adjusted to pH 9.66 at 60° C.

is 9.66 at 60° C.; Rhodes and Bascom found that a solution with a pH of 10.7 at room temperature showed the greatest efficiency.

To solutions containing 0.25 per cent of the soap were added known amounts of the following salts: disodium phosphate, dipotassium phosphate, sodium sulfate, sodium tetraborate, sodium chloride, and sodium acetate. To each mixed solution a dilute solution of sodium hydroxide was added until the adjusted pH of the final solution, at 60° C., was at the optimum value. With each solution, washing tests were made. In each case two samples of soiled fabric were washed together through four washes, and measurements were made as described. In some instances completely independent duplicate washing experiments were made. Since the results of such completely independent experiments agreed as closely as did the results obtained when the duplicate samples were washed together, the completely independent washing experiments were not made in every instance. The average deviation between the results of the duplicate experiments was usually not greater than  $\pm 0.5$  per cent; in the series of washings made with sodium sulfate the arithmetical average deviation was  $\pm 1.0$  per cent.

The addition of the simple inorganic salts of sodium (chloride, sulfate, and phosphate) causes first an increase and then a decrease in the detergent power of the soap solution. With all three of these salts the optimum concentration is about 5 milligram equivalents per liter. The effect of the added salt appears to be about proportional to the valence of the anion. Potassium phosphate in very low concentrations appears to decrease the effectiveness of the soap; larger concentrations decrease the detergent power. The optimum concentration of potassium phosphate is much higher than that of sodium phosphate; at this optimum

concentration the potassium salt is less effective than is the sodium salt at its optimum concentration.

Some of these observed facts are in agreement with the generally accepted theories of the structure and behavior of soap solutions; some can be explained only by hypotheses that have little or no independent substantiation. It is generally assumed that the detergent action of soap is due primarily to the adsorption of micellar aggregates of the anions of the soap or of un-ionized molecules of the acid soap on the particles of dirt. The addition of the simple inorganic salts of sodium in relatively small concentrations, by increasing the agglomeration of the ions into micellar aggregates, should increase the activity of the soap and enhance its detergent action. This effect may be ascribed primarily to the anions of the added salt; as is to be expected, it increases with increase in the valence of the anion. The action of larger concentrations in decreasing the detergent action may be due to the effect of the added sodium salt in depressing the ionization of the soap; it may also be due in part to the excessive agglomeration of the colloidal soap particles in very large micelles that are less effective in peptizing the dirt.

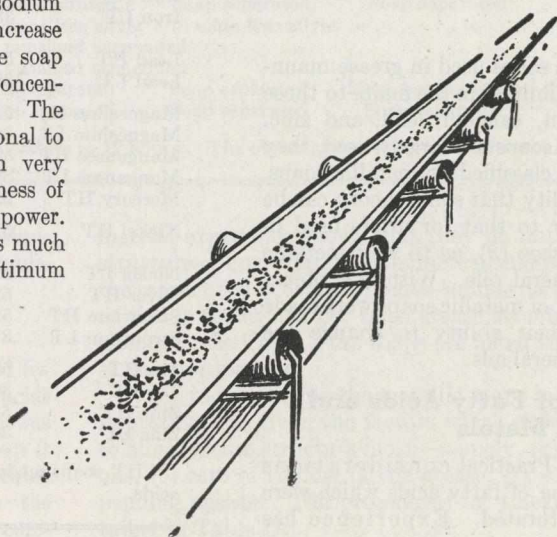
The results appear to indicate that the potassium cations have a specific effect in decreasing the detergent action of the soap. Conceivably the potassium ion may decrease the tendency toward the formation of active micelles; more probably, perhaps, the potassium ions may diminish the effective adsorption on the particles of soil. That the final decrease in the detergent power with increasing salt concentration appears at a higher concentration with potassium phosphate than with sodium phosphate suggests, but does not prove, that in both cases the decrease is due to the decrease in the solubility of the soap rather than to a specific effect of the added anion.

It is conceivable that the action of acetates and borates in decreasing the washing effect may be due to the adsorption of acetate and borate ions on the particles of dirt, with consequent decrease in the adsorption of the more effective anions of the soap. There is no independent proof of this hypothesis.

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RECEIVED June 26, 1936.



# Metallic Soaps for Thickening Mineral Oils

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Eighteen metals were combined with two fatty acids of different titer to form metallic soaps. These soaps were heated to the same temperature with two mineral oils and cooled to find whether grease resulted. Grease was formed with soaps from nine of the metals. These nine, with the exception of aluminum, were divalent or gave divalent compounds.

Soaps of the metals with the lowest atomic weights produced greases of best transparency. In general, soaps of the more basic metals produced the softest greases. Water as an emulsifier was not required except in the case of calcium and strontium soaps.

The consistency was heaviest and the dropping point highest in greases made from the highest titer acid. Behavior of the metallic soaps in both naphthenic- and paraffin-base oils with a Saybolt viscosity of 100 at 100° F. was similar.

**T**HE metallic soaps used in grease manufacture are limited, in the main, to those of aluminum, calcium, lead, and zinc. Although sodium soaps are largely used, they are not generally classified as metallic soaps. There is a possibility that some theory can be developed, similar to that for driers used in paints and varnishes (2), as to why metallic soaps thicken mineral oils. With this object in view, a number of metallic soaps were made and tested for their ability to change the consistency of mineral oils.

## Selection of Fatty Acids and Metals

**FATTY ACIDS.** Practical considerations led to the selection of fatty acids which were predominantly saturated. Experience has

determined that the most desirable calcium-base greases result from the use of a mixture of oleic, palmitic, and stearic acids of a titer of 32 to 44. Acids of lower titer give soft greases, and with higher titer smoothness is sacrificed. Similarly, in the manufacture of greases with aluminum soaps, aluminum stearate provides the greatest thickening whereas the oleate tends to give a more fluid grease. Likewise, lead stearate gives a grease of much heavier body than the oleate or naphthenate.

Thus the acids used—namely, double-pressed stearic acid and lard fatty acids—fall in the classification of those largely used in practice.

**METALS.** Since all but a very small fraction of lubricating greases are manufactured from aluminum, calcium, lead, and sodium, the first three of

TABLE I. PROPERTIES OF METALLIC SOAPS

Metallic Soap <sup>a</sup>	Metal			Appearance of Metallic Soaps
	Titer of Acids	Washed Ash, %	Soluble Ash, %	
Aluminum HT	52.13	4.01	0.21	Fluffy white powder
Aluminum LT	38.05	4.02	0.37	Cream powder, fuses about 220° F.
Barium HT	52.13	18.71	Not detd.	White powder
Barium LT	38.05	19.96	Not detd.	Cream powder
Cadmium HT	52.13	16.23	Not detd.	White powder
Cadmium LT	38.05	15.15	Not detd.	Cream powder
Calcium HT	52.13	10.82	0.11	White fluffy powder
Calcium LT	38.05	10.78	0.24	Cream powder
Cerium HT	52.13	6.80	0.16	Light yellow dense powder
Cerium LT	38.05	6.79	0.58	Yellow mass, fuses about below 200° F.
Chromium HT	52.13	6.82	0.14	Blue-green powder, fuses about 210° F.
Chromium LT	38.05	6.00	0.36	Dark green mass, fuses below 200° F.
Cobalt HT	52.13	8.45	0.29	Purple powder
Cobalt LT	38.05	8.23	0.42	Brownish purple mass, fuses below 200° F.
Copper HT	52.13	10.05	0.26	Fluffy blue-green powder
Copper LT	38.05	9.05	0.45	Green mass, fuses below 200° F.
Iron HT	52.13	7.45	0.00	Fluffy red-brown powder
Iron LT	38.05	5.86	0.70	Dark red-brown mass, fuses below 180° F.
Lead HT	52.13	22.33	Not detd.	White powder
Lead LT	38.05	22.20	Not detd.	Cream powder, fuses about 200° F.
Magnesium HT	52.13	4.18	0.01	White fluffy powder
Magnesium LT	38.05	4.36	0.17	White powder, fuses about 210° F.
Manganese HT	52.13	8.81	0.13	Cream powder, pink tinge
Manganese LT	38.05	8.55	0.70	Brown mass, fuses below 200° F.
Mercury HT	52.13	20.09	..	White powder
Nickel HT	52.13	9.13	0.37	Light green powder, fuses about 210° F.
Nickel LT	38.05	8.99	0.02	Dark green, fuses below 200° F.
Silver HT	52.13	15.86	..	White powder
Strontium HT	52.13	23.60	..	White powder
Strontium LT	38.05	23.49	..	Cream powder, fuses about 220° F.
Tin HT	52.13	16.58	0.10	Cream powder, fuses below 220° F.
Tin LT	38.05	16.50	0.31	Yellow mass, fuses below 180° F.
Zinc HT	52.13	11.60	0.10	White powder
Zinc LT	38.05	11.50	0.18	White powder

<sup>a</sup> HT soaps made from double-pressed stearic acid; LT soaps from lard fatty acids.

TABLE II. CHARACTERISTICS OF METALLIC SOAP DISPERSIONS IN MINERAL OILS<sup>a</sup>

Soap	10% of Soap Heated to 260° F. in Oil with Viscosity of 100 at 100° F.		10% of Soap Heated to 230° F. in Oils as Before; 0.5% Water Added, Stirring until Mixture Cooled to 200° F.		10% of Soap + 0.5% of Stearic Acid Heated in Oils as Before to 260° F.	
	Naphthenic oil	Paraffin oil	Naphthenic oil	Paraffin oil	Naphthenic oil	Paraffin oil
Aluminum HT	Clear firm gel	Clear firm gel	Not as clear or as firm as dry mixture	Not as clear or as firm as dry mixture	Clear firm gel	Clear firm gel
Aluminum LT	Clear rubbery gel	Clear rubbery gel	Same	Same	Clear rubbery gel	Clear rubbery gel
Barium HT	Under no conditions was a homogeneous mixture obtained even at 330° F. where soap fused to a clear mass					
Barium LT	No homogeneous mixture obtained in any instance					
Cadmium HT	Opaque firm gel	Opaque firm gel	Soft gel syneresis	Soft gel syneresis	Opaque firm gel	Opaque firm gel
Cadmium LT	Opaque semi-fluid	Opaque semi-fluid	Soap in lower 75% of oil	Soap in lower half of oil	Semi-fluid syneresis	Semi-fluid syneresis
Calcium HT	Most of soap separated	Most of soap separated	Opaque gel	Opaque gel	Most of soap separated	Most of soap separated
Calcium LT	Solid soap structure throughout but oil could be poured from this		Opaque gel	Opaque gel	Most of soap separated	Most of soap separated
Cerium HT	Soap separated in lower 90% of oil	Soap separated in lower 65% of oil	Soap separated	Soap separated	Most of soap separated	Most of soap separated
Cerium LT	Soap separated	Soap separated	Soap separated	Soap separated	Most of soap separated	Most of soap separated
Chromium HT	Soap separated, oil colored	Soap separated, oil colored	Soap separated	Soap separated	Soap separated	Soap separated
Chromium LT	Soap separated, oil colored	Soap separated, oil colored	Soap separated	Soap separated	Soap separated	Soap separated
Cobalt HT	Firm gel, translucent	Firm gel, translucent	Nonuniform gel	Nonuniform gel	Firm gel	Firm gel
Cobalt LT	Livery gel, translucent	Livery gel, translucent	Nonuniform gel	Nonuniform gel	Livery gel	Livery gel
Copper HT	Soap separated, oil colored	Soap separated, oil colored	Soap separated	Soap separated	Soap separated	Soap separated
Copper LT	Soap separated, oil colored	Soap separated, oil colored	Soap separated	Soap separated	Soap separated	Soap separated
Iron HT	Soap separated, oil colored	Soap separated, oil colored	Soap separated	Soap separated	Soap separated	Soap separated
Iron LT	Soap separated, oil colored	Soap separated, oil colored	Soap separated	Soap separated	Soap separated	Soap separated
Lead HT	Opaque firm mass, softens on working	Opaque firm mass, softens on working	Firm mass	Firm mass	Firm mass	Firm mass
Lead LT	Soap suspended mass would barely flow	Semi-fluid syneresis	Semi-fluid	Semi-fluid	Semi-fluid	Semi-fluid
Magnesium HT	Clear firm gel	Clear firm gel	Soft gel	Soft gel	Firm gel	Firm gel
Magnesium LT	Clear viscous liquid	Clear viscous liquid	Cloudy liquid	Cloudy liquid	Viscous liquid	Viscous liquid
Manganese HT	Soap separated	Soap separated	Soap separated	Soap separated	Soap separated	Soap separated
Manganese LT	Soap separated, oil colored	Soap separated, oil colored	Soap separated	Soap separated	Soap separated	Soap separated
Mercury HT	Firm mass, opaque	Firm mass, opaque	Firm mass, some free Hg	Firm mass, some free Hg	Firm mass	Firm mass
Nickel HT	Firm gel, translucent	Firm gel, translucent	Firm gel, cloudy	Firm gel, cloudy	Firm gel	Firm gel
Nickel LT	Viscous liquid clear	Viscous liquid clear	Cloudy liquid	Cloudy liquid	Viscous liquid	Viscous liquid
Strontium HT	Fluid, no separation	Fluid, no separation	Opaque firm mass	Opaque firm mass	Soap separated	Soap separated
Strontium LT	Soap separated	Soap separated	Opaque firm mass	Opaque firm mass	Soap separated	Soap separated
Silver HT	Soap separated	Soap separated	Soap separated, some free silver	Soap separated, some free silver	Soap separated	Soap separated
Tin HT	Mixtures did not clear at 260° F. but soap remained suspended					
Tin LT	Mixtures did not clear at 260° F. but soap remained suspended					
Zinc HT	Soap separated	Soap separated	Soap separated	Soap separated	Mass becoming semi-fluid when touched	
Zinc LT	Soap separated	Soap separated	Soap separated	Soap separated	Soap separated	Soap separated

<sup>a</sup> After heating, the mixtures were cooled slowly to room temperature in 12 hours. The observations were made after 24 hours.

these metals were used, together with others which have similar characteristics or occur in like groups in the periodic table.

### Experimental Procedure

Soaps were made by double decomposition as outlined by Whitmore and Lauro (8). One hundred grams of fatty acids were used in the manufacture of each lot of soap which was thoroughly washed; but with the resulting bulk of soap it was difficult to free the product entirely from water-soluble impurities. Although such impurities may influence the thickening action of the metallic soaps in mineral oils, com-

mercial experience shows that they do not prevent a grease structure. For example, commercial aluminum stearate on the market today contains water-soluble material, and, as long as this is under one per cent, grease structure is not greatly affected. In Table I the soaps are listed together with some of their properties.

When incorporating the metallic soaps in mineral oils, consideration was given the factors which experience has shown to affect grease structure most—namely, (a) different mineral oils, (b) rate of cooling of the grease, (c) emulsifying or suspending agents. The procedures for thickening oils are detailed in Table II.

TABLE III. PROPERTIES OF LUBRICATING GREASES MADE FROM METALLIC SOAPS

Metallic Soap	Appearance of Grease	Consistency <sup>a</sup> Unworked	Dropping Point <sup>b</sup> ° C. (° F.)	Syneresis after 30 Days	Comments
Aluminum stearate <sup>c</sup>	Light brown, clear	205	83 (181)	None	...
Aluminum, low titer <sup>c</sup>	Dark brown, clear	270	70 (158)	None	Rubbery nature
Cadmium stearate <sup>c</sup>	Light brown, opaque	200	85 (185)	None	...
Cadmium, low titer <sup>c</sup>	Semi-fluid, opaque	Too soft	Too soft	None	...
Calcium stearate <sup>d</sup>	Cream, opaque	260	95 (203)	None	...
Calcium, low titer <sup>d</sup>	Cream, opaque	290	92 (198)	None	...
Cobalt stearate <sup>c</sup>	Purple, translucent	180	75 (167)	None	...
Cobalt, low titer <sup>c</sup>	Purple, translucent	Too soft	Too soft	About 5% free oil	Same characteristics in both dry and moist mixtures
Lead stearate <sup>c</sup>	Light yellow, opaque	130	83 (181)	None	...
Magnesium stearate <sup>c</sup>	Yellow, clear	265	75 (167)	None	...
Magnesium, low titer <sup>c</sup>	Yellow, clear	Too soft	Too soft	...	Clear viscous liquid, 225 Saybolt viscosity at 100° F.
Nickel stearate <sup>c</sup>	Green, translucent	230	65 (149)	None	...
Nickel, low titer <sup>c</sup>	Green, clear	Too soft	Too soft	...	Clear liquid, 150 Saybolt viscosity at 100° F.
Mercury stearate <sup>c</sup>	Cream, opaque	260	107 (225)	About 3 % free oil	Grainy appearance
Strontium stearate <sup>d</sup>	Cream, opaque	260	102 (216)	None	...
Strontium, low titer <sup>d</sup>	Yellow, opaque	275	77 (171)	None	...

<sup>a</sup> A. S. T. M. method D 217, 33 T.

<sup>b</sup> Holde, "The Examination of Hydrocarbon Oils and of Saponifiable Fats and Waxes," tr. by Mueller, p. 189, New York, John Wiley & Sons, 1915.

<sup>c</sup> Grease made by heating 10% of dry soap in oil 100 viscosity (at 100° F.) to 260° F. and cooling slowly.

<sup>d</sup> Grease made by heating 10% of dry soap in oil of 100 viscosity (at 100° F.) to 230° F., then adding 0.5% water and stirring the mixture until the temperature dropped to 200° F.

### Discussion of Results

Of eighteen metals combined with fatty acids, nine gave metallic soaps which, in turn, produced lubricating greases that were worthy of consideration. Although the entire metal field was not covered, indications are that divalent combinations furnish the most promising and satisfactory bases for lubricating greases. Five of the metals—magnesium, calcium, strontium, cadmium, and mercury—in group II of Mendeleeff's periodic arrangement of the elements, are divalent. Three others—cobalt, lead, and nickel—form divalent compounds. The remaining metal, aluminum, according to McBain and McClatchie (?), does not furnish a trivalent soap but rather a mono- or divalent. Further, Licata (6) says: "It is believed by some that the value of aluminum stearate as a suspension agent depends on its free stearic acid content. Various types of aluminum stearate are made. The type with a high stearic acid content forms thin gels. The low stearic acid type forms thick gels." Faragher and associates (3) go so far as to state that aluminum monooleate gives a much heavier body in mineral oil than either the dioleate or trioleate.

Referring to Table II, soaps of four metals—aluminum, cobalt, magnesium, and nickel—gave greases which were clear or translucent; the soaps of cadmium, calcium, lead, mercury, and strontium gave opaque greases. The first four are metals of comparatively low atomic weight and thus the metal content of their soaps is low; probably, therefore, a low percentage of metal in soaps used in lubricating greases will tend to give a more transparent or translucent grease structure.

Study of the consistencies of greases obtained (Table III), indicates that the more basic the metal the softer the consistency of the thickened mineral oil. Likewise, the greases made from soaps containing high-titer acids were always heavier in consistency than the low-titer combinations. In view of these results, the statements of two authors may be of interest. Klimont (5) is of the opinion that the solubility of the metallic soaps depends on the melting point of the concerned fatty acids. Licata (6) states: "While the fatty acid radical to a large extent governs the physical properties of a metallic soap, the metallic fraction determines the chemical

properties. In general it can be said that solubility decreases from naphthenates, linoleates, oleates, palmitates to stearates, which are least soluble. Aluminum stearate seems to be the exception to this rule." In the series of metals reported on here no greater difficulty was experienced in obtaining greases with stearic acid soaps than with lard fatty acid soaps.

Only with calcium and strontium soaps was water necessary to hold the soap in suspension. With most other soaps, 0.5 per cent of water tended to break down the structure. This result does not entirely agree with Fischer (4) who found that water-combining ability in metallic soap gels depended on the metallic radical decreasing from magnesium, calcium, mercury, and lead to barium.

On all greases made, the dropping point was highest with fatty acid combinations of the highest titer.

Soaps which formed a grease in naphthenic-base oil would also give a grease in paraffin-base oil. The latter produces a little less opaque grease, but the difference in consistency was not appreciable.

This paper covers preliminary data on this question, and further work will be undertaken.

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RECEIVED May 7, 1936. Presented before the Division of Petroleum Chemistry at the 91st Meeting of the American Chemical Society, Kansas City, Mo., April 13 to 17, 1936.



# Chemical Reactions in Fertilizer Mixtures

## Effect of Ammoniation on Urea Component of Superphosphate Mixtures

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THE use of free ammonia in the preparation of fertilizer mixtures is now a common practice in the fertilizer industry. The ammonia is added in the aqueous or anhydrous form or as an ammonia solution of urea or other nitrogenous material (9). The addition of ammonia to a fertilizer mixture is accompanied by a rise in the temperature of the mass, due mainly to the heat developed in the reactions between the free ammonia and the superphosphate in the mixture.

The extent of this increase in temperature and its effect upon the availability of the phosphorus and other characteristics of the product have been investigated by others (5, 11). The effect upon urea present during ammoniation has not been previously studied; it was the purpose of the present investigation to ascertain whether urea decomposes under conditions that obtain during ammoniation of superphosphate and to determine the extent and nature of such decomposition.

Temperatures in excess of 60° C. are probably seldom reached in the commercial ammoniation of mixtures containing ordinary superphosphate. When double superphosphate

is substituted for the ordinary grade and relatively larger amounts of ammonia are added, as might be done in the preparation of high-analysis mixtures, higher temperatures would no doubt be reached. Even in extreme cases, however, the evaporation of moisture would prevent temperatures much in excess of 100° C. from being reached; that temperature was therefore chosen as the upper limit in the present investigation.

### General Method

The problem was attacked in two ways. In the first and most extensive series of experiments, mixtures of urea and ammoniated superphosphate, containing varying amounts of urea, ammonia, and water, were heated at constant temperature for periods from several hours to a number of days. The course of the reactions was followed by determining the amounts of ammonia and of carbon dioxide that were evolved. In order to determine the causes of the urea decomposition in superphosphate mixtures, the rate of decomposition of pure urea was compared in the same way and under similar conditions with the rate of decomposition of urea mixed with pure

The heat developed during the ammoniation of superphosphate, or of mixtures containing it, may cause the urea present to decompose or hydrolyze by reaction with various substances if temperatures in excess of 50° C. are maintained for several days. The carbon dioxide formed during the decomposition escapes from the mixture, but the ammonia is in general retained by the acidic constituents except on prolonged heating at higher temperatures. Only 4 to 8 per cent of the urea was decomposed on heating a urea-superphosphate mixture at 60° C. for 100 hours, but extensive decomposition occurred at 80° C. and all the urea was hydrolyzed after a few hours at 100° C.

Mixtures containing double superphosphate behave in a similar way to those containing ordinary superphosphate. A

study of urea phosphate and of mixtures of urea with the individual components of superphosphate indicated that the hydrolysis of urea occurs by reaction with free water, water of crystallization, or with the water of constitution of monocalcium phosphate, monoammonium phosphate, dicalcium phosphate, or phosphoric acid. Ammonium and calcium sulfates and tricalcium phosphate were found to have little or no effect on the urea hydrolysis.

Experiments on the decomposition of urea in complete fertilizers showed that some slight decomposition may occur on prolonged heating at temperatures as low as 45° C. In one sample complete decomposition occurred on heating 4 weeks at 65° C. More than 50 per cent of the urea in all samples decomposed the first week at 85° C.

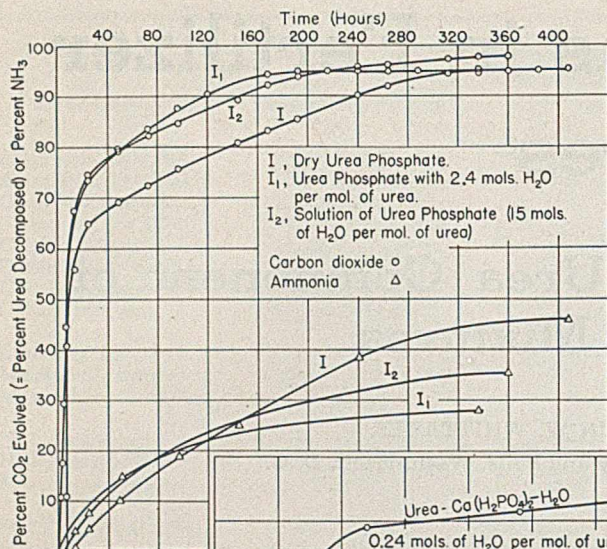
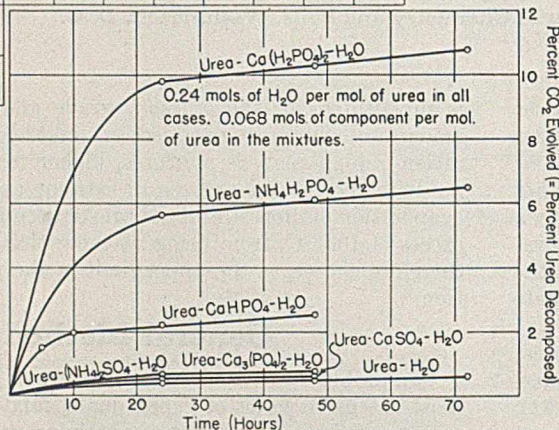


FIGURE 1 (Left).  
DECOMPOSITION  
OF UREA  
PHOSPHATE AT  
100° C.

FIGURE 2 (Right).  
DECOMPOSITION  
OF UREA ALONE  
AND MIXED WITH  
VARIOUS COMPONENTS  
OF SUPER-  
PHOSPHATE



compounds which are, or may be, the components of ammoniated superphosphate-urea mixtures. The compounds studied included ammonium sulfate, calcium sulfate, monoammonium phosphate, and mono-, di-, and tricalcium phosphates. Urea phosphate [ $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_3\text{PO}_4$ ] was also tested, since it may be present in mixtures initially containing urea and monocalcium phosphate as the writers have recently shown (13, 14).

In the second series of experiments the decomposition of urea contained in four complete mixtures was studied by making direct determinations of the amount of urea present before and after heating at various temperatures.

## The Effect of Superphosphate and Its Components on Urea Decomposition

The apparatus and procedure used were as follows:

A charge of approximately 30 grams of the sample to be studied was spread in a thin layer on the bottom of a 250-cc. Erlenmeyer flask equipped with inlet and outlet tubes sealed in on opposite sides just below the neck. The flask was closed by a ground-glass stopper during the early runs, but later the neck of the flask was sealed after the sample was inserted. The flask was placed in a drying oven, the temperature of which was constant to  $\pm 1^\circ \text{C}$ . with the inlet and outlet tubes extending through the wall of the oven. The apparatus was arranged in triplicate so that runs could be made at 100°, 80°, and 60° C., simultaneously.

A stream of air, purified by successive passage through soda lime, Ascarite, and 25 per cent sulfuric acid solution, was passed over the sample in the flask at a rate of about 30 cc. per minute to carry off ammonia, carbon dioxide, and other volatile matter. The amount of ammonia evolved was determined by passing the air through 48 per cent sulfuric acid and distilling the ammonia from an aliquot part of the acid in the usual way. Slightly high results were obtained in some cases, due probably to sublimation of urea from the flask into the acid used to absorb the ammonia.

The gases leaving the ammonia absorption bubbler were

freed from water by passage through concentrated sulfuric acid and Dehydrite; then the carbon dioxide was determined by absorption in Ascarite.

## Analytical Methods

Phosphorus pentoxide and total nitrogen were determined by the volumetric molybdate and Gunning methods, respectively. Urea was determined by the urease method (4, 15). Experiments have shown that this method does not distinguish uncombined urea from additive compounds such as  $\text{CaSO}_4 \cdot 4\text{CO}(\text{NH}_2)_2$  (12) or urea phosphate,  $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_3\text{PO}_4$ . Moisture was determined in the ammoniated superphosphate mixtures by means of a modified Bidwell-Sterling apparatus (2), using benzene as the boiling liquid. Figures so obtained probably represent the total "free" water plus part of the water of crystallization (6). This method, however, appeared to be the one most suitable for use in the presence of urea, and values so obtained are sufficiently accurate for present purposes. The water content of the moistened urea and of the mixtures of urea with the various components of superphosphate was computed from the water added plus water of crystallization, if present. The latter was included because of the tendency of urea to set free water of crystallization (12, 14). Qualitative tests for pyro-, meta-, and orthophosphates were made by the use of zinc sulfate, albumin solution acidified with acetic acid, and molybdate solution, respectively, under the proper conditions.

## Materials

The urea, ammonium sulfate, monoammonium phosphate, calcium sulfate dihydrate, and ammonium hydroxide used in the tests were c. p. grade. The urea phosphate was prepared by the method of Matignon, Dode, and Langlade (8) and was recrystallized from alcohol. The monocalcium phosphate monohydrate, dicalcium phosphate dihydrate, and tricalcium phosphate were of the Schering-Kahlbaum analytical grade. Monocalcium phosphate was recrystallized from phosphoric acid solution by the method of Clark (3) and washed carefully with alcohol and ether. The tricalcium phosphate analyzed as follows:

$\text{P}_2\text{O}_5$	44.67%
CaO	48.65
$\text{CO}_2$	None
$\text{H}_2\text{O}$ (at 105° C.)	1.33
Total loss in weight at 1000° C.	6.51

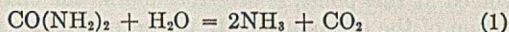
The superphosphate and double superphosphate used in preparing the ammoniated mixtures were commercial materials manufactured from Florida pebble rock. They analyzed as follows:

	Superphosphate	Double Superphosphate
Water-sol. $\text{P}_2\text{O}_5$	17.50%	42.24%
Citrate-insol. $\text{P}_2\text{O}_5$	0.08	0.08
Total $\text{P}_2\text{O}_5$	20.40	48.86
Free $\text{H}_3\text{PO}_4$ (titration of acetone extract)	1.76	5.11

## Urea and Ammoniated Superphosphate Components

Dry urea is known to be stable up to its melting point (132° C.) (10) but may sublime at much lower temperatures. Above the melting point, decomposition occurs with the formation of biuret, ammonia, ammelide, and cyanuric acid. Such temperatures were not attained in the present investiga-

tion, however, and it has been assumed throughout this paper that the urea hydrolyzed according to Equation 1:



Where urea decomposition is referred to, its hydrolysis is meant regardless of the actual source of the water. Wherever the expressions "per cent carbon dioxide" or "per cent ammonia" are used, the percentage evolved of that potentially present in the urea used is meant. "Per cent carbon dioxide" then becomes equal to the percentage of urea hydrolyzed or decomposed. The percentage of ammonia could not be used as a measure of the urea decomposition since in general some part of it was retained by reaction with constituents of the mixtures studied.

In order to determine the extent to which the various compounds present influence the decomposition of urea at elevated temperatures, the hydrolysis of urea alone was compared with that of urea in urea phosphate and with urea in various mixtures containing urea and one of the other compounds which may be present in mixtures of urea and ammoniated superphosphate. The decomposition of urea alone was studied at 60°, 80°, and 100° C., and that of the other materials at 100° C. only. Various initial moisture contents were used in the cases of urea and urea phosphate. In all mixtures a moisture content of 0.24 mole of water per mole

of urea was used, and in all but one mixture (sample F<sub>1</sub>), which contained an excess of monoammonium phosphate, an excess of urea was employed.

The results of these experiments with the exception of those on urea decomposition at 60° and 80° C. are collected in Table I and plotted in Figures 1 and 2. Some of these results are used later in discussing the effect of varying water content (Figure 9). The decomposition of urea alone takes place very slowly at 60° and 80° C. with 2 per cent of water present at the start.

TABLE I. CARBON DIOXIDE AND AMMONIA EVOLVED FROM UREA, UREA PHOSPHATE, AND MIXTURES OF UREA WITH THE COMPONENTS OF AMMONIATED SUPERPHOSPHATE AT 100° C.

Sample	Admixed Material	H <sub>2</sub> O/Urea Mole ratio	Time of Heating Hours	CO <sub>2</sub> %	NH <sub>3</sub> %
H <sub>2</sub>	.....	0.07	24	0.17	0.16
			48	0.40	0.38
H <sub>3</sub>	.....	0.24	24	0.42	0.55
			48	0.52	0.68
H <sub>4</sub>	.....	1.00	24	2.07	...
			46.75	3.26	4.24
H <sub>5</sub>	.....	15.00	24	4.74	...
			48	9.03	9.84
Urea Phosphate					
I	.....	Dry	24	64.71	4.50
			48	69.11	10.07
			360	94.94	...
			408	95.46	45.94
I <sub>1</sub>	.....	2.34	24	73.52	...
			48	79.18	17.0
			336	94.93	27.95
			648	94.91	32.44
I <sub>2</sub>	.....	15.00	24	74.48	7.80
			48	79.56	...
			336	97.68	...
			360	97.68	35.42
Mixtures <sup>a</sup>					
E	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	0.24	24	0.67	0.73
F	NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	0.24	24	5.65	2.30
			48	6.11	3.47
			552	11.48	10.10
F <sub>1</sub>	Excess NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	3.73	216	6.47	4.57
G	Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub>	0.24	24	9.79	4.10
			48	10.27	5.53
L	CaHPO <sub>4</sub>	0.24	24	2.20	...
			48	2.53	2.58
M	CaSO <sub>4</sub>	0.24	24	0.57	...
			48	0.60	0.79
N	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	0.24	24	0.66	...
			48	0.73	1.09

<sup>a</sup> The mole ratio of H<sub>2</sub>O to the added compound was 3.538, and that of the added compound to urea was 0.068 except in sample F<sub>1</sub>. Water of crystallization, if present, was included when calculating the mole ratio of water to urea.

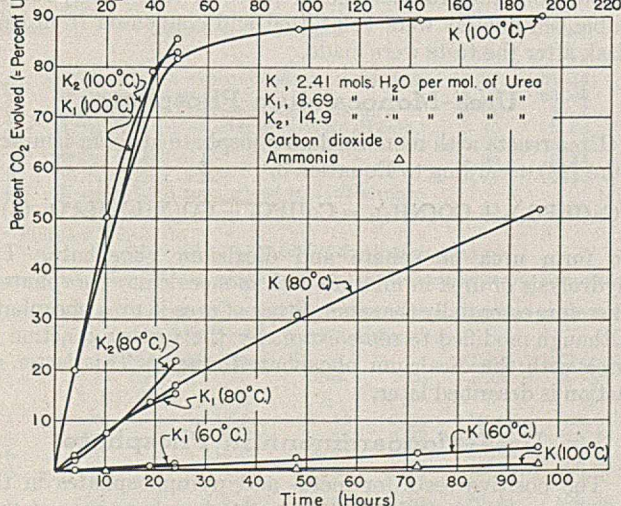
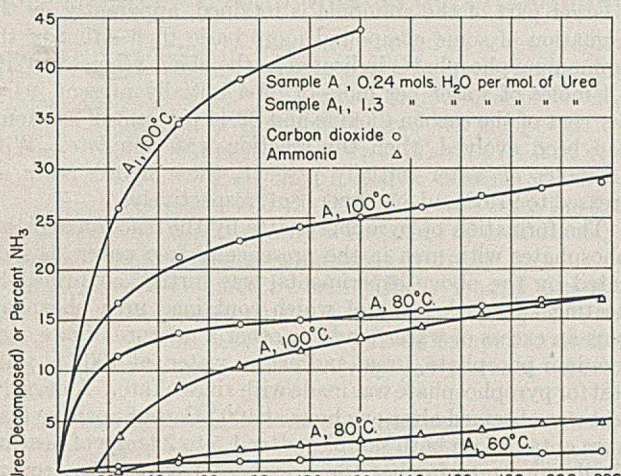


FIGURE 3 (Upper). DECOMPOSITION OF UREA IN AMMONIATED SUPERPHOSPHATE MIXTURES CONTAINING EXCESS UREA AT 60°, 80°, AND 100° C.

FIGURE 4 (Lower). EFFECT OF VARYING WATER CONTENT ON DECOMPOSITION OF UREA IN A SUPERPHOSPHATE MIXTURE AMMONIATED WITH UREA-AMMONIA SOLUTION

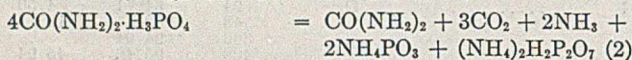
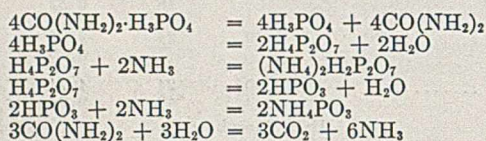
Three of the compounds studied—ammonium sulfate, tricalcium phosphate, and calcium sulfate—apparently have little or no effect on the urea hydrolysis. Of the other three compounds, monocalcium phosphate has the greatest accelerating effect on the hydrolysis, with monoammonium phosphate and dicalcium phosphate about one-half and one-fourth as much, respectively, as judged by the percentage of urea decomposed after 24 hours. The results obtained are discussed in more detail in the following paragraphs.

### Urea Phosphate

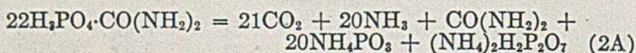
Table I and Figures 1 and 9 show that the amount of urea hydrolyzed in dry urea phosphate after heating 24 hours at 100° C. was about 650 times the hydrolysis occurring in pure dry urea; but that when 15 moles of water were present per mole of urea, the rate of hydrolysis of urea phosphate was about

16 times as great as that of urea containing an equivalent amount of water.

Dry urea phosphate decomposed completely in about 360 hours at 100° C., as judged by the fact that no further gas was evolved. At this time 94.9 per cent of the carbon dioxide and 45 per cent of the ammonia potentially present had been liberated, and 4.2 per cent of the urea present was found to have sublimed into the upper part of the reaction flask and in the exit tubing. The sample liquefied on prolonged heating at 100° C., whereas the melting point of urea phosphate is 117.5° C. (8). Moreover the residue gave positive tests for both pyro- and metaphosphate but no test for orthophosphate. In view of these facts it is suggested that the decomposition may be regarded as having taken place in several steps as follows: The urea phosphate first dissociated into free phosphoric acid and urea, and the orthophosphoric acid thus liberated lost water to form pyro- and meta- acids. The water from this dehydration reacted with the urea which resulted in the formation of carbon dioxide and ammonia, and part of the latter combined with the pyro- and metaphosphoric acids. The following series of known reactions is suggested:



According to this scheme the urea cannot be completely hydrolyzed unless all the phosphate is converted to the meta state; otherwise sufficient water is not available. By writing Equation 2 with 22 molecules of urea phosphate and one of diammonium pyrophosphate it is possible to account almost exactly for the results obtained:



Such an equation indicates that 95.45 per cent of the carbon dioxide and 45.45 per cent of the ammonia should have been evolved, leaving 4.55 per cent of undecomposed urea.

The change of direction of the carbon dioxide curve (Figure 1, I) between 50 and 60 per cent decomposition indicates a

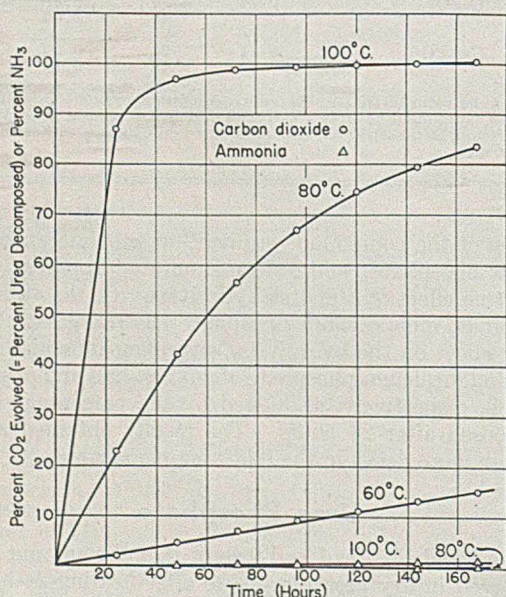


FIGURE 5. DECOMPOSITION OF UREA IN A SUPERPHOSPHATE AMMONIATED WITH UREA-AMMONIA SOLUTION (SAMPLE C)

change in the nature of the reactions. Since about half the urea had decomposed and very little ammonia had been evolved at this point, it probably marks the end of the conversion of the orthophosphate to the pyro state as indicated by the first three reactions of the above scheme. The subsequent dehydration of the pyrophosphoric acid proceeded more slowly, as indicated by the slope of the curve. The actual urea hydrolysis could occur only as the water became available, and the evolution of ammonia over the more nearly horizontal portion of the curve is evidence that the formation of metaphosphate was the principal reaction during that interval. Sufficient water for the observed hydrolysis could have been supplied only by nearly complete dehydration to the meta state. The results for initially dry urea show that no significant amount of hydrolysis occurred by reaction with the water vapor in the air stream passed over the samples.

It has been stated that at 180° C. urea phosphate decomposes to form ammonium metaphosphate exclusively (8), and the formation of both pyro and meta acids at 100° C. would, therefore, not be surprising since the pyro acid may be considered an intermediate step in the complete dehydration of the ortho acid to form metaphosphoric acid. When orthophosphoric acid is heated alone, the meta acid starts to form at 180° C. (1). In the presence of urea the dehydration is probably accelerated, the water being withdrawn more rapidly by the urea hydrolysis to form carbon dioxide and ammonia.

When free water is present initially in the urea phosphate, a larger part of the ammonia is retained, apparently by the formation of some compound more basic than either of the ammonium phosphates indicated in the above scheme. With 2.4 moles of water per mole of urea initially present, 94.91 per cent of the carbon dioxide and 32.44 per cent of ammonia had been evolved when the reaction was complete. With 15 moles of water initially present, these figures were increased to 97.68 and 35.42 per cent, respectively.

The formation of pyrophosphates by the reaction of orthophosphates with urea in the presence of free water, as indicated by the above experiments, was further confirmed by heating two flasks, one of which contained urea phosphate plus an excess of water, and the other a mixture of monoammonium phosphate, urea, and excess water, at 100° C.; the test for pyrophosphate was made with zinc sulfate. A negative test was obtained after one hour at 100° C., but positive tests were obtained on both samples after 1.5 to 2 hours of heating. To demonstrate further the presence of free water, several cubic centimeters were volatilized and condensed from each flask after the tests were made.

### Urea-Monocalcium Phosphate

Urea reacts with monocalcium phosphate at room temperature (14) according to Equation 3,



to form urea phosphate and dicalcium phosphate. The hydrolysis of urea in mixture with monocalcium phosphate is therefore essentially the same as that of urea in urea phosphate, although modified to some extent by the further reaction of urea with the dicalcium phosphate formed. This latter reaction is described later.

### Urea-Monoammonium Phosphate

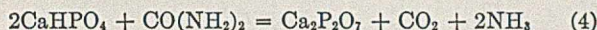
The positive tests for meta- and pyrophosphates in the residue and the negative test for orthophosphate suggest that the decomposition of urea in the presence of monoammonium phosphate proceeded along much the same lines as with urea phosphate. An additional mixture was run containing an excess of ammonium phosphate instead of excess urea. This resulted in the evolution of all of the carbon dioxide and 71.21



per cent of the ammonia potentially present. Here also the retention of a part of the ammonia by some compound more basic than ammonium metaphosphate or diammonium pyrophosphate is indicated.

### Urea-Dicalcium Phosphate

The ordinary tests for meta- and pyrophosphates were unsatisfactory with the residues from the urea-dicalcium phosphate mixtures. In order to determine whether all of the phosphorus present was in the ortho state, P<sub>2</sub>O<sub>5</sub> was precipitated as ammonium phosphomolybdate from a solution of the residue, both before and after warming with nitric acid. More phosphorus was precipitated after this treatment. Equal fractions of the carbon dioxide and ammonia potentially present were evolved (Table I), indicating that no ammonia was absorbed. These observations suggest the following reaction:



When dicalcium phosphate is in excess of that necessary to react as in Equation 4, the excess should undergo ammoniation at the temperature of these experiments with the resultant formation of tricalcium phosphate and monoammonium phosphate (11) and thus reduce the loss of ammonia.

### Urea Mixed with Ammoniated Superphosphate

The decomposition of urea was studied in seven ordinary superphosphate mixtures and in one mixture that contained double superphosphate. The initial composition of the mixtures, their method of preparation, and the composition of the superphosphates used are given in Table II. The composition of three of these mixtures after heating at various temperatures is shown in Table III. In some cases the final composition was used to verify the amount of urea decomposition indicated by the carbon dioxide evolved.

Sample A was prepared by mixing finely ground urea with previously ammoniated superphosphate, and sample A<sub>1</sub> was prepared by adding water to A. These samples contained a large excess of urea over that required to react with the

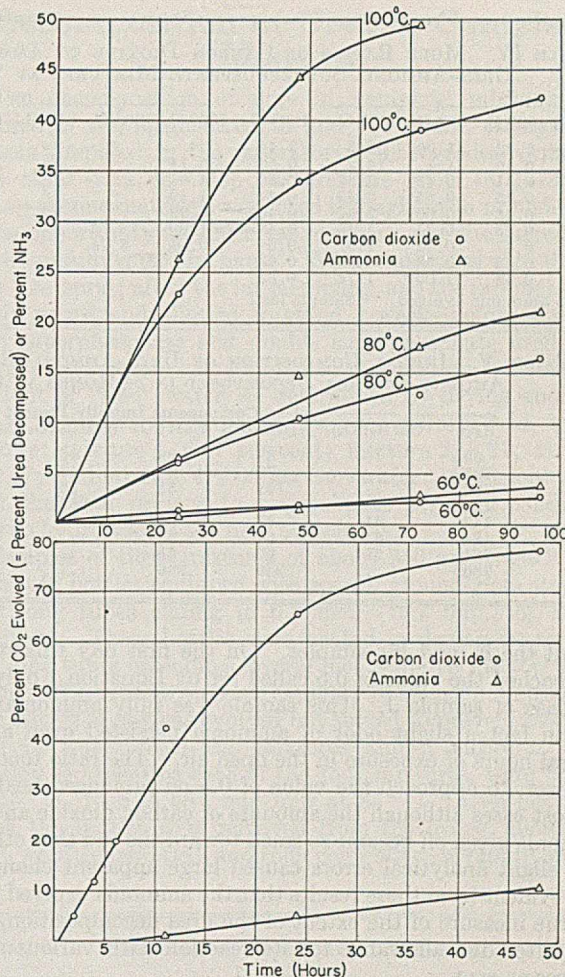


FIGURE 6 (Upper). DECOMPOSITION OF UREA IN A SUPERPHOSPHATE MIXTURE SATURATED WITH AMMONIA (SAMPLE J)

FIGURE 7 (Lower). DECOMPOSITION OF UREA AT 100°C. IN A DOUBLE SUPERPHOSPHATE AMMONIATED WITH UREA-AMMONIA SOLUTION (SAMPLE O)

TABLE II. INITIAL COMPOSITION OF UREA-AMMONIA-SUPERPHOSPHATE MIXTURES

Sample	Method of Preparation	Total N %	Urea %	NH <sub>3</sub> <sup>a</sup> %	H <sub>2</sub> O <sup>b</sup> %	Total P <sub>2</sub> O <sub>5</sub> %	H <sub>2</sub> O/Urea <sup>b</sup> Mole ratio
A	Urea added to ammoniated superphosphate	14.02	24.86	2.94	1.77	14.91	0.24
A <sub>1</sub>	Water added to A	13.00	23.05	2.73	8.93	13.82	1.29
C	Ammoniated with urea-NH <sub>4</sub> OH soln.	3.94	3.18	2.99	14.40	16.53	14.95
J	Extra NH <sub>3</sub> added after urea-NH <sub>4</sub> OH soln.	8.36	3.58	8.17	2.98	17.79	2.77
K	Ammoniated with urea-NH <sub>4</sub> OH soln.	2.39	3.57	0.88	2.56	19.65	2.39
K <sub>1</sub>	Water added to K	2.24	3.34	0.82	8.72	18.41	8.69
K <sub>2</sub>	Water added to K	2.11	3.15	0.78	14.07	17.33	14.90
O	Urea-NH <sub>4</sub> OH soln. added to double superphosphate	7.92	6.32	4.97	13.3	39.19	7.01

<sup>a</sup> Inorganic ammonia.

<sup>b</sup> Water as determined by the Bidwell-Sterling apparatus.

TABLE III. COMPOSITION OF UREA-AMMONIA-SUPERPHOSPHATE MIXTURES AFTER HEATING

Sample	Temp. °C.	Period of Heating Days	Total N %	Urea %	NH <sub>3</sub> %	Total P <sub>2</sub> O <sub>5</sub> %	Urea N Lost <sup>a</sup> %
A	100	9	12.99	17.54	5.85	16.49	36.24
A	80	9	14.38	21.62	5.22	15.92	18.54
A	60	9	14.42	24.99	3.36	15.42	2.81
A <sub>1</sub>	100	9	8.58	3.49	8.45	18.26	88.53
C	100	7	4.80	None	5.84	20.41	100.00
C	80	7	4.82	0.65	5.50	20.25	83.45
C	60	7	4.32	3.03	3.55	18.31	14.60
J	80	4	8.28	3.28	8.01	18.78	14.35
J	60	4	8.41	3.66	8.15	17.66	....

<sup>a</sup> Per cent of urea nitrogen initially present converted to inorganic ammonia but not necessarily evolved (includes the slight amount of urea sublimed).

various compounds present. All the other samples were prepared by ammoniating superphosphate with urea-ammonium hydroxide solutions of varying concentrations to give products of the desired composition. Samples K<sub>1</sub> and K<sub>2</sub> were prepared from K by the addition of water. Additional anhydrous ammonia was added to J after ammoniating with urea-ammonium hydroxide solution in order to secure the

desired high concentration of ammonia. In sample O, double superphosphate was used instead of ordinary superphosphate. In no case was the temperature allowed to rise above 40° C. during ammoniation. As is shown later, no urea decomposition should occur at that temperature.

The mixtures when first made were more moist in appearance than after standing for several days in tightly stoppered glass containers. This indicates that a part of the free moisture had become fixed as water of hydration.

The results obtained on heating these mixtures are plotted in Figures 3 to 7, inclusive, and the mole ratios of carbon dioxide to ammonia evolved each day are given in Table IV for

TABLE IV. MOLE RATIOS OF CARBON DIOXIDE TO AMMONIA EVOLVED EACH DAY FROM UREA-AMMONIA-SUPERPHOSPHATE MIXTURES AT VARYING TEMPERATURES

Day (24 Hr.)	A			A <sub>1</sub> 100° C.	C			J			K <sub>1</sub> 100° C.	O <sub>1</sub> 100° C.
	100° C.	80° C.	60° C.		100° C.	80° C.	60° C.	100° C.	80° C.	60° C.		
1	2.46	11.96	62.5	3.45	a	a	a	0.44	0.46	0.85	a	6.40
2	0.46	1.1	14.2	0.50	35.14	a	a	0.31	0.27	0.39	9.66	1.08
3	0.41	0.45	2.37	0.50	4.61	a	a	0.47	0.40	0.15	1.31	
4	0.45	0.55	2.43	0.44	1.19	a	a	b	0.49	0.20	1.15	
5	0.43	0.63	2.37	0.46	0.99	a	a					
6	0.43	0.35	1.45	0.48	1.00	12.75						
7	0.41	0.42	1.97	0.54	0.84	8.74						
8	0.46	0.53	0.93	0.68								
9	0.44	1.06	1.71	0.62								

<sup>a</sup> No ammonia evolved. <sup>b</sup> Sample lost.

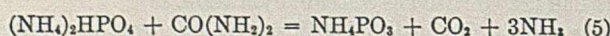
TABLE V. INITIAL COMPOSITION OF UREA-AMMONIA-SUPERPHOSPHATE MIXTURES AND AMOUNT OF UREA DECOMPOSED IN 24 HOURS AT 100° C. (IN MILLIMOLES)

Sample	Components Initially Present							Urea	Urea Decomposed
	H <sub>2</sub> O	Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub>	NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub>	CaHPO <sub>4</sub>	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	CaSO <sub>4</sub>		
A	99	..	82	28	46	41	222	414	68
A <sub>1</sub>	495	..	76	26	42	38	206	384	99
C	798	..	101	51	36	35	266	53	46
J	165	..	..	..	255	99	57	60	14
K	142	64	67	64	..	..	347	60	48
K <sub>1</sub>	484	61	64	61	..	..	331	56	46
K <sub>2</sub>	781	57	60	58	..	..	312	52	45
O	736	..	286	236	..	3	2	105	60

all but the K<sub>1</sub> and K<sub>2</sub> samples. On the first day this ratio approached the value of 0.5 called for by Equation 1 only in the case of sample J. This sample was fully ammoniated, and in fact a slight odor of ammonia persisted even after several hours of exposure in the open air. The ratio tended, however, to approach the value of 0.5 on prolonged heating in most cases although the amounts of carbon dioxide and of ammonia given off became so small toward the end that otherwise slight analytical errors caused large apparent changes. It is evident from these results that the ammonia evolved was no true measure of the extent of the urea decomposition, except after due allowance for its reaction with various substances present.

Keenan (?) showed that the components of ammoniated ordinary superphosphate vary with the degree of ammoniation; White, Hardesty, and Ross (11) did the same for double superphosphate. From the data of these workers it was possible, after making due allowance for the urea and water present, to compute the number of millimoles of each component present in the urea-superphosphate mixtures studied (Table V). In all except the A samples, the amounts of the reacting components were greatly in excess of those of the urea, and practically complete decomposition of the urea would therefore be expected. This was actually obtained at 100° C., except in the fully ammoniated sample, J.

In order to arrive at the amounts of the various components present in sample J, some extrapolation of Keenan's curves was necessary. This indicated the entire absence of those compounds previously shown to be active in effecting the decomposition of urea. It is probable, however, as suggested by Keenan, that heavily ammoniated superphosphates ammoniated at low temperatures contain diammonium phosphate, the presence of which in sample J was also indicated by the persistent faint odor of ammonia after long exposure to the air. This sample is the only one in which the ammonia evolved exceeded that called for by Equation 1. It is suggested that the urea decomposition observed in this case was due either to reaction of the urea with diammonium phosphate according to Equation 5 or to the straight decomposition of diammonium phosphate to form ammonia and monoammonium phosphate and subsequent reaction of the urea with the latter:



Either of these reactions would produce the observed excess of ammonia.

The decomposition of urea therefore occurs by reaction with other ammoniated superphosphate components even though monocalcium phosphate, the compound most active in decomposing it, is entirely absent as it was in all except the K samples. When the urea is not in excess, practically complete decomposition can be expected after 24 to 48 hours of heating at 100° C. (except in fully ammoniated samples), regardless of the particular components present. About the same considerations would seem to apply to double superphosphate.

### Minimum Temperature of Urea Decomposition

When the percentage of urea decomposed after a definite interval is plotted against the temperature (Figure 8), the resultant curves, when extrapolated to zero per cent decomposition, indicate the minimum temperature of urea decomposition. This temperature, for urea-ammoniated superphosphate mixtures, is about 57° C. unless the curves become markedly asymptotic as they closely approach the temperature axis. The results on complete mixtures, described later, indicate that such is perhaps the case since slight decomposition was noted on prolonged heating at 45° C. Probably no decomposition of urea should occur during the ammoniation of superphosphate mixtures unless temperatures in excess of about 50° C. are maintained for long periods. Above this temperature, urea may be decomposed with loss of carbon dioxide from the mixture but this decomposition is not necessarily accompanied by loss of ammonia. Figures 3, 4, and 5 show that, although some ammonia may be lost on continued heating, this loss does not become appreciable under 24 hours at the temperatures studied, except in the case where excess urea is present. In superphosphate, which has not been fully ammoniated, the ammonia can be absorbed in various ways (?)—for example, by the reaction:

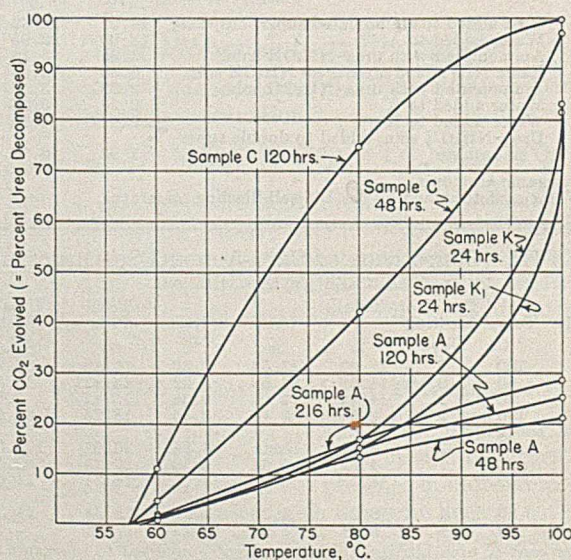
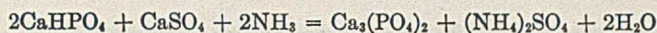


FIGURE 8. MINIMUM TEMPERATURE OF UREA DECOMPOSITION



The fully ammoniated sample (Figure 6) and the double superphosphate containing 4.97 per cent ammonia (Figure 7) showed that significant losses of ammonia occurred much sooner. It seems safe, however, to say that no loss of ammonia should occur in the usual practice where the ammoniation of ordinary superphosphate is stopped short of saturation, unless a high temperature is maintained for several days.

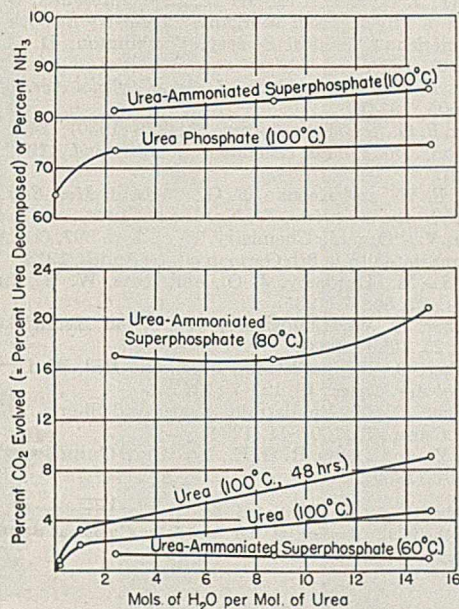


FIGURE 9. EFFECT OF WATER ON DECOMPOSITION OF UREA, OF UREA PHOSPHATE, AND OF UREA IN A UREA-SUPERPHOSPHATE MIXTURE (K SAMPLES) AMMONIATED WITH UREA-AMMONIA SOLUTION

All values for 24 hours except as noted

Although allowing the temperature of a superphosphate-urea mixture to remain above  $50^\circ\text{C}$ . for an extended period does not necessarily entail actual loss of ammonia, it does mean extensive conversion of organic into inorganic ammonia. The urea ammonia appears to be converted into salts of ortho-, meta-, or pyrophosphoric acids.

### Effects of Varying Water Content

Figure 9 shows how the amount of water initially present affects the urea hydrolysis. Although urea and urea phosphate hydrolyze much more rapidly when the water increases from 0 to 1 or 2 moles per mole of urea, further increase in the amount of water up to 15 moles per mole of urea has a relatively slight effect on the amount of hydrolysis occurring in 24 hours. The water initially present in the superphosphate mixtures had a similarly large influence when increased from 0.24 to 1.29 moles per mole of urea (samples A and A<sub>1</sub>, Figure 3), but over the range from 2.4 to 15 moles little change was noted. Since 2.4 to 15 moles of water per mole of urea includes the range of water content variation normally occurring in superphosphate mixtures, it is evident that initial water content is not an important factor. This is also illustrated in Figure 4 where the rates of decomposition of urea in three mixtures differing only in initial water content are given. For the first 24 hours the curves practically coincide and probably would have continued to do so if extended farther on the time axis. During the hydrolysis, the urea may react with water initially present as water of constitution, of crystallization, or as free water.

## Decomposition of Urea in Complete Mixtures

The decomposition of urea in complete mixtures was studied in two single-strength and two double-strength fertilizers prepared in the laboratory. The grades, formulas, and other data on these mixtures are given in Table VI. Finely ground materials were used throughout to provide optimum opportunity for chemical reaction, and the ingredients were carefully mixed by hand. Water was added with the aid of a fine spray after the initial mixing, and the products were again mixed and allowed to stand 2 weeks before analysis. The superphosphate and double superphosphate used were ammoniated before being added to the mixture. The initial content of "free" water, as determined by drying about 50 hours in an evacuated desiccator over sulfuric acid, was as follows: mixture 1, 6.97 per cent; mixture 2, 6.81; mixture 3, 6.17; and mixture 4, 6.05 per cent water. Sufficient water was therefore present to approximate practical conditions and to hydrolyze all the urea completely.

Samples of these mixtures of about 250 grams each were placed in bottles equipped with special ground-glass stoppers and long tubes ending in 0.5 inch (12.7 mm.) of 1-mm. capillary. These bottles were heated in drying ovens with the long tubes extending several inches above the top of the oven. The tubes with their capillary openings permitted the free escape of any gas evolved but served to prevent evaporation of water from the mixtures almost entirely. Four bottles, representing each of the four mixtures, were heated at  $45^\circ\text{C}$ ., four at  $65^\circ$ , and four at  $85^\circ\text{C}$ . After heating 1 week the bottles were removed from the ovens, allowed to cool, weighed, emptied, and their contents were rapidly mixed,

TABLE VI. FORMULAS OF COMPLETE MIXTURES CONTAINING UREA

Material	Single-Strength Mixtures (4-8-4)		Double-Strength Mixtures (8-16-8)	
	No. 1	No. 2	No. 3	No. 4
Superphosphate, 19.6% P <sub>2</sub> O <sub>5</sub>	816	816	...	686
Double superphosphate, 46.7% P <sub>2</sub> O <sub>5</sub>	...	...	686	686
Ammonia, 3% of superphosphate	24	24	...	...
Ammonia, 7.2% of double superphosphate	...	...	48	48
Ammonium sulfate, 20.8% N <sub>2</sub>	144	144	288	288
Sodium nitrate, 16.3% N <sub>2</sub>	61	61	122	122
Urea, 46.6% N <sub>2</sub>	43	43	86	86
Potassium chloride, 50% K <sub>2</sub> O	159	159	318	318
Dolomite, 95%	226	None	452	None
Filler (quartz sand)	527	753	...	452
	2000	2000	2000	2000

TABLE VII. PERCENTAGE OF UREA IN COMPLETE MIXTURES BEFORE AND AFTER HEATING AT VARIOUS TEMPERATURES<sup>a</sup>

Time of Heating Weeks	Mixed Fertilizer			
	No. 1	No. 2	No. 3	No. 4
	Before Heating			
0	2.0	2.0	4.0	4.0
	After Heating at $45^\circ\text{C}$ .			
1	1.9	1.9	3.7	3.6
2	1.8	1.8	3.8	3.8
3	1.6	1.8	3.6	3.8
4	1.6	1.8	3.8	3.7
	After Heating at $65^\circ\text{C}$ .			
1	1.7	1.3	2.9	1.5
2	1.4	0.7	2.3	1.6
3	1.1	0.2	2.1	1.4
4	1.1	0.0	2.2	1.2
	After Heating at $85^\circ\text{C}$ .			
1	0.7	0.2	1.8	1.5
2	0.5	0.0	1.7	0.9
3	0.3	0.0	1.2	0.4
4	0.2	0.0	1.1	0.4

<sup>a</sup> Calculated on the basis of unheated mixtures.

sampled, and quickly returned to the bottles which were reweighed and heated another week, when the operation was repeated. All bottles were heated 4 weeks.

The maximal loss in weight noted after heating a week was 1.73 per cent lost by one sample at 85° C. during the first week. The average loss per week per sample was 0.51 per cent, which indicated that the tubes extending above the oven tops effectively reduced evaporation.

Inorganic ammonia and urea plus inorganic ammonia were determined by the method of Yee and Davis (15) in the mixtures before heating and in all the weekly samples. One-half gram of material was weighed directly into the special distillation flasks, and 5 cc. of water were added before either distilling the ammonia off or digesting with urease. Because of the relatively large amounts of ammonia present, it was necessary to use a more concentrated alcoholic caustic solution than that specified by Yee and Davis.

As a further check on any possible loss in weight of the mixtures, either during the heating or the mixing, total  $P_2O_5$  determinations were also made on the mixtures before heating and on all weekly samples. The results obtained for the urea content were then corrected to the basis of the original material, using the  $P_2O_5$  content as a reference figure. These corrections were small.

The results are given in Table VII. Some decomposition of urea occurred even at 45°, and in one sample at 65° C. the urea was completely destroyed in 4 weeks. The decomposition was very rapid at 85° C. These results are, in general, what would be expected from the data on urea-superphosphate mixtures and show that these data are applicable to complete mixtures.

### Acknowledgment

Thanks are due to J. O. Hardesty for preparation of the ammoniated samples.

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RECEIVED July 18, 1936. Presented before the Division of Fertilizer Chemistry at the 92nd Meeting of the American Chemical Society, Pittsburgh, Pa., September 7 to 11, 1936.

# Increasing the Effective Life of Razor Blades

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WHEN safety razor blades are used with a brushless type of shaving cream, they become dull much more quickly than with a brush type of cream. Examination of both types of cream showed that the pH value of the brushless type was 7.2, while that of the brush type was 9.4. Since oxygen corrosion of steel occurs readily at a pH of 7.2 but is appreciably retarded at a pH of 9.4, the theory was formulated that the dulling of razor blades was due to oxygen corrosion during the process of shaving. An accelerated corrosion test was made by placing a new razor blade, that could be stropped, free from its paraffin coating, between the folds of a piece of cloth wet with a mixture of 20 grams of the brushless shaving cream and 80 cc. of water. The cloth with the razor blade was supported on the bottom of a beaker inverted in a larger beaker containing the mixture of shaving cream and water, the ends of the cloth extending down into the liquid so that the cloth was continuously wet with the liquid. Thus the razor blade was kept wet with water from the mixture and at the same time was in contact with air. The larger beaker was covered with a watch glass. Each day the blade was dried, stropped twenty-five double strokes, and replaced between the folds of the

cloth. The condition of the cutting edge of the blade at the end of 7 days is shown by Figure 1.

A similar test was carried out at the same time using the brush type of shaving cream with a pH of 9.4. The condition of the edge of the razor blade in this test at the end of 7 days is shown by Figure 2.

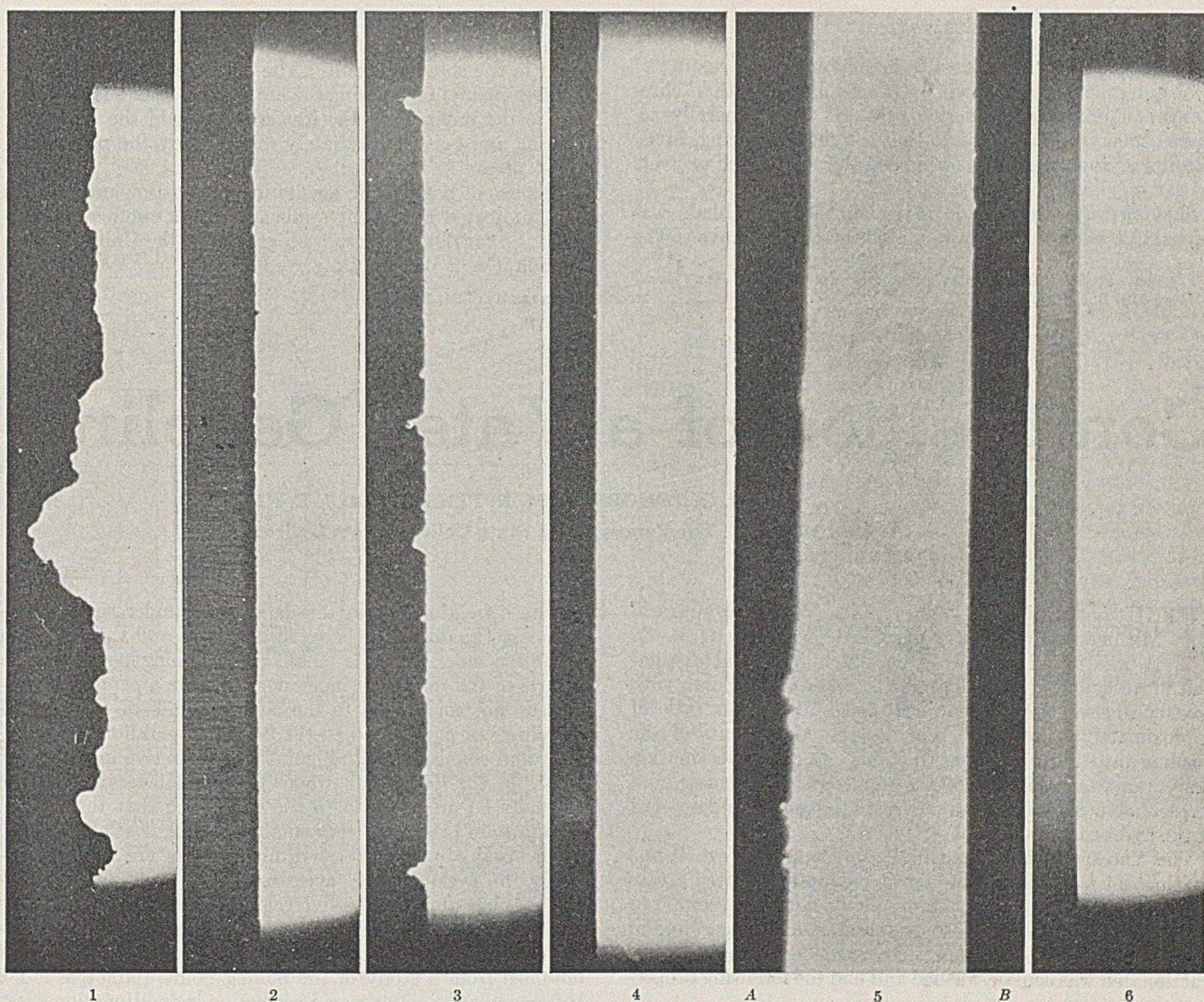
Determinations were made of the pH of various brushless and brush-type shaving creams on the market. The results are as follows:

Shaving Cream	Type	pH
Burma-Shave	Brushless	7.2
Mennen's	Brushless	8.2
Barbasol	Brushless	8.1
Glider	Brushless	7.5
Colgate	Brush	9.2
Williams	Brush	9.4
Palmolive	Brush	9.2

A series of accelerated corrosion tests was made with these shaving creams, with results similar to those shown in Figures 1 and 2.

### Effect of Potassium Chromate

With the idea of retarding the corrosion of razor blades during shaving, potassium chromate was added to a commercial brushless shaving cream with a pH of 7.2. The potassium chromate did not change the pH value. Figure 3 shows the condition of the cutting edge of the blade after shaving tests



FIGURES 1 TO 6. PHOTOMICROGRAPHS ( $\times 105$ ) OF RAZOR BLADE EDGES

- |   |  |
|---|--|
| <ol style="list-style-type: none"> <li>1. Accelerated corrosion test with 7.2-pH shaving cream</li> <li>2. Accelerated corrosion test with 9.4-pH shaving cream</li> <li>3. Untreated brushless type shaving cream of 7.2 pH</li> </ol> | <ol style="list-style-type: none"> <li>4. Treated brushless type shaving cream of 7.2 pH</li> <li>5. Untreated (A) and treated (B) brush type shaving cream of 9.2 pH</li> <li>6. New blade used in comparative shaving tests</li> </ol> |
|---|--|

with the untreated cream, and Figure 4 shows the cutting edge used with the chromate-treated cream.

A similar shaving test was made using a commercial brush type shaving cream with a pH of 9.2, first as sold on the market and then when chromate-treated. The potassium chromate did not change the pH value. The condition of the cutting edge of the blades is shown by Figure 5.

Figures 3 and 5A show that corrosion of the cutting edge occurs when the blades are used with shaving creams of 9.2 pH as well as with creams of 7.2 pH. Figures 4 and 5B show that the addition of potassium chromate to shaving creams having a pH value of 9.2 as well as to creams with a pH of 7.2 materially retards the corrosion of razor blades used with them.

Similar comparative shaving tests were made with two other brushless types and one other brush type of shaving cream on the market. The effect on the cutting edge of razor blades was similar to the results shown in Figures 3, 4, and 5.

In making comparative shaving tests, new razor blades of the same brand were used and were cleaned and dried immediately after use. Figure 6 is typical of the cutting edge of the new razor blades tested. Each blade was used an equal num-

ber of times by the same person. The number of times a blade was used with untreated shaving cream was carried beyond the point of comfortable shaving.

Five men, using different makes of razor blades, were given a supply of a brushless type of shaving cream, as sold on the market, with a pH of 7.2, and another supply of the same cream to which potassium chromate had been added. These men, starting with new razor blades, noted the number of shaves they obtained with a blade before it became dull and had to be discarded. All reported that they obtained a greater number of shaves with the chromate-treated shaving cream than with the shaving cream as sold on the market. The increase in the number of shaves varied from 50 to 200 per cent.

Razor blades used with chromate-treated shaving creams have been in service without cleaning or drying and without reducing the number of satisfactory shaves obtained with a blade, in comparison with the number obtained when the blade was cleaned and dried in the customary manner. Shaving creams containing a chromate salt in an amount sufficient to inhibit oxygen corrosion have been used by several hundred men without a case of skin irritation.

### Passivation

The action of chromate salts in inhibiting the rusting of steel is termed "passivation." Other substances than chromates can produce passivation of steel. The generally accepted theory of the action is that a tightly adhering, invisible film of an iron oxide is formed on the steel which protects it.<sup>1</sup>

Shaving tests were made in which the razor blade was dipped in a solution of a chromate salt after each shave. The

<sup>1</sup> Speller, F. N., "Corrosion, Causes and Prevention," New York, McGraw-Hill Book Co., 1926.

results in lengthening the effective life of razor blades were not as satisfactory as when the chromate salt was incorporated in the shaving cream. The effectiveness of the treated shaving cream in increasing the life of razor blades is probably due to the breaking of the iron oxide film in the process of shaving and being immediately reformed by the passivating agent present.

The use of passivating agents in shaving preparations has been protected by patent applications in a number of countries. So far patents have been granted in the United States, Canada, Great Britain, Italy, and France.

RECEIVED April 24, 1936.

# Composition of a Yates Gasoline

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THE constitution of Pennsylvania, West Virginia, and Michigan gasolines was discussed previously (1, 6, 7).

It was found that a single batch fractional distillation of 45 gallons (170 liters) of a gasoline in a column with seventy to seventy-five theoretical plates at a reflux ratio of approximately 40 to 1 will separate the constituents of the gasoline into narrow-boiling fractions. Such a fractionation enables us to classify different gasolines and to speculate with a reasonable degree of assurance as to the nature and amount of the hydrocarbons present.

The Yates pool is located in Pecos County, West Texas, and in 1935 was the eighth largest pool in the United States (4). The gasoline has a relatively high octane number, 60 to 64 A. S. T. M., and is sometimes used as a base gasoline in making fuels of high octane number. The gasoline to be fractionated was caustic-washed and had the following properties:

A. S. T. M. Engler Distillation, ° F. (° C.)					
Initial b. p.	108 (42)	50%	294 (146)	A. P. I. gravity	54.9
10%	186 (86)	60%	314 (157)	Octane No. (procedure 345)	60
20%	223 (106)	70%	335 (168)	Reid vapor pressure at 100° F. (38° C.), lb.	7
30%	250 (121)	80%	356 (180)	Sulfur content, %	0.24
40%	272 (133)	90%	380 (193)		
		End point	410 (210)		

The fractionation was made in the column previously described (7), with the exception that, because of minor changes, the column had the equivalent of seventy to seventy-five theoretical plates when tested under total reflux with a mixture of *n*-heptane and methylcyclohexane. Forty-five gallons were charged into the still and fractionated at an average reflux ratio of 35 to 1. The gasoline was accordingly divided into 180 fractions, each fraction consisting of 0.3 to 0.6 per cent of the charge. The average boiling spread (initial boiling point to 50 per cent point) as determined in a modified Cottrell boiling point apparatus was 0.2° C. (0.4° F.) although some fractions were obtained with a zero spread. A material balance follows:

	Vol. % of Charge
Noncondensable gas	2.5
Distillate	66.0
Residue	24.7
Hold-up and loss	6.8
Total	100.0

The results of the fractionation are given in Figure 1 and Tables I to IV. This gasoline differs markedly from other

gasolines fractionated in this laboratory under similar conditions. The difference between the peaks and valleys in the refractive index curve is small. The boiling points of the valleys of the refractive index curve, unlike a paraffinic gasoline, do not correspond to the boiling points of the normal paraffins but correspond to the branched paraffins. In fact, the rapid change of boiling point and refractive index at the points in the distillation where the normal paraffins would normally be present lead to the conclusion that the normal paraffins are present in very small amounts, if at all.

The peaks in the refractive index curve are due, respectively, to cyclopentane, cyclohexane at 80.4° C., methylcyclohexane at 101.7°, ethylcyclohexane at 130.4°, a non-naphthene, cumene, and a naphthene at 152.3°, and trimethylbenzenes at about 170° C. These conclusions were obtained from a study of the boiling point, refractive index before and after sulfuric acid extraction, refractionation data, octane number, and the experience gained in fractionating a large number of gasolines of various types.

Since there are appreciable differences in refractive index among normal paraffins, branched paraffins, and naphthenes,

A fractional distillation of 45 gallons (170 liters) of a Yates straight-run gasoline run in a standardized manner yielded considerable information regarding its constitution. The gasoline was found to differ from other gasolines of paraffin type. A study of the fractions obtained showed that the gasoline consists mainly of naphthenes and branched paraffins. Methylcyclohexane and ethylcyclohexane were isolated and identified. No normal paraffins were found. Aromatic hydrocarbons are present in but negligible amounts below 157° C. (315° F.). However, certain fractions, with a lower refractive index and density than other fractions, have higher octane numbers.

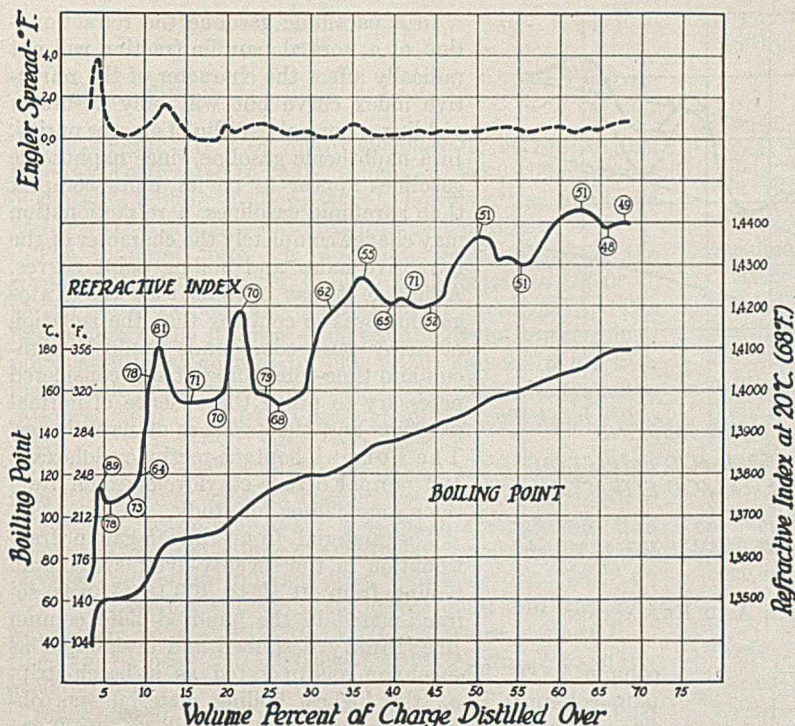


FIGURE 1. FRACTIONATION OF A YATES STRAIGHT-RUN GASOLINE  
The numbers in circles are octane numbers obtained according to procedure 345.

the refractive index after acid extraction is a possible indication of the type of hydrocarbons present. Although this extraction with acid may not quantitatively remove aromatic hydrocarbons higher than benzene, and there also may be reaction with certain hydrocarbon types other than aromatics, nevertheless experience with this procedure has shown it to be valid for at least qualitative purposes. Figure 2 compares the Yates gasoline fractions before and after sulfuric acid extraction at room temperature and indicates the presence of naphthenes. The concentration of aromatic hydrocarbons below 157° C. (315° F.) is very low. No benzene was found and the maximum concentration of toluene in any one fraction was 1.5 volume per cent, of xylenes and ethylbenzene 3.4 per cent, and of nine-carbon aromatics 4 per cent.

The behavior of the refractive index and boiling point curves indicates the gasoline to be extremely complex. Above 138° C. (280° F.) the boiling point curve rises steadily with none of the breaks characteristic of a paraffinic gasoline. No fraction was obtained with physical constants close to those of a pure substance.

### Octane Numbers

The octane number curve is of particular interest. The usual paraffinic type gasoline has its highest octane number fractions at the peaks of the refractive index curve. The Yates gasoline, however, in several instances has higher octane numbers in the valleys of the refractive index curve than at the peaks. It so happens that among the lower boiling hydrocarbons the highly branched, high-antiknock paraffins boil close to the aromatic hydrocarbons. Therefore in a gasoline containing aromatic hydrocarbons, since aromatic hydrocarbons have a high refractive index, the fractions at the peaks of the refractive index curve have high octane numbers. In a naphthenic type gasoline with a low or negligible concentration of aromatics, the peaks in the refractive index curve are due to naphthenes whose boiling points, except for cyclohexane, are different from the aromatics, and consequently the high-antiknock fractions are located in the valleys of the refractive index curve. In the

higher boiling range the number of branched paraffins and naphthenes present is so great that with normal paraffins and aromatics present only in small amounts, a great difference in octane number between the peaks and the valleys would not be expected. The high octane number of the first peak in the refractive index curve is due to the high blending octane number of cyclopentane itself. The high octane number of the second peak is due to the fact that methylcyclopentane, cyclohexane, benzene, and the highly branched heptanes have approximately the same boiling point. The previously expressed statement (?) that in many cases the apparent parallelism between refractive index and density curves and knock rating does not exist is supported by the octane-number curve of the Yates gasoline.

Unlike a paraffinic gasoline, the Yates gasoline maintains a reasonably high octane number even in the high-boiling fractions; in the low-boiling fractions it does not exhibit the extreme changes in octane number characteristic of a paraffinic gasoline. These effects substantiate the distillation data regarding the absence of normal paraffins. The octane number and tetraethyllead susceptibility of certain blends made from the fractions obtained on distillation were recently published (8).

### Refractionation

The value of efficient fractionation in the separation of the constituents of petroleum has been emphasized (2). Although

TABLE I. ORIGINAL FRACTIONS CONTAINING MAXIMUM AND MINIMUM CONCENTRATION OF AROMATIC HYDROCARBONS

Vol. % of Charge Distilled	B. P., 760 Mm.		Refractive Index, $n_D^{20}$		Estd. Aromatics %
	° C.	° F.	Before acid extrn.	After acid extrn.	
4.4	52.8	127.0	1.3770	1.3770	0.0
5.4	...	...	1.3732	1.3732	0.0
10.5	72.4	162.3	1.4030	1.4030	0.0
11.5	80.4	176.7	1.4105	1.4105	0.0
15.3	90.5	194.9	1.3970	1.3970	0.0
20.3	99.2	210.6	1.4132	1.4132	0.0
21.3	101.7	215.1	1.4190	1.4179	1.3 <sup>a</sup>
21.9	103.1	217.6	1.4171	1.4159	1.9 <sup>a</sup>
27.7	117.2	243.0	1.4078	1.4078	0.0
32.8	121.4	250.5	1.4207	1.4208	0.0
34.5	124.7	256.9	1.4230	1.4228	0.0
35.8	130.4	266.7	1.4270	1.4228	5.8 <sup>b</sup>
39.7	136.0	276.8	1.4209	1.4182	3.4 <sup>b</sup>
46.3	145.5	293.9	1.4246	1.4240	0.8 <sup>b</sup>
49.2	150.4	302.7	1.4351	....	..
50.2	152.3	306.1	1.4369	1.4348	4.0 <sup>c</sup>
55.2	160.0	320.0	1.4300	1.4222	10.3 <sup>c</sup>
61.4	168.4	335.1	1.4425	1.4352	11.0 <sup>c</sup>
64.6	174.6	346.3	1.4407	....	..

<sup>a</sup> Toluene.

<sup>b</sup> Xylenes and ethylbenzene.

<sup>c</sup> Nine-carbon aromatics.

TABLE II. FRACTIONS OF NARROW BOILING RANGE FROM YATES GASOLINE

Known Hydrocarbons of Similar Boiling Point	Vol. % of Charge Distilled	Boiling Range ° C.	Boiling Spread ° C.
n-Hexane	1.4	65-72	7
Benzene	2.1	72-87	15
Isomeric heptanes	6.1	87-92	5
n-Heptane	0.5	96-99	3
Isomeric octanes	8.3	114-123	9
n-Octane	1.1	123-128	5
Xylenes	7.8	128-140	12
Isomeric nonanes	5.3	140-148	8
n-Nonane	1.1	148-151	3
Cumene	2.9	151-157	6
Isomeric decanes	11.5	157-172	15
n-Decane	1.0	172-174	2

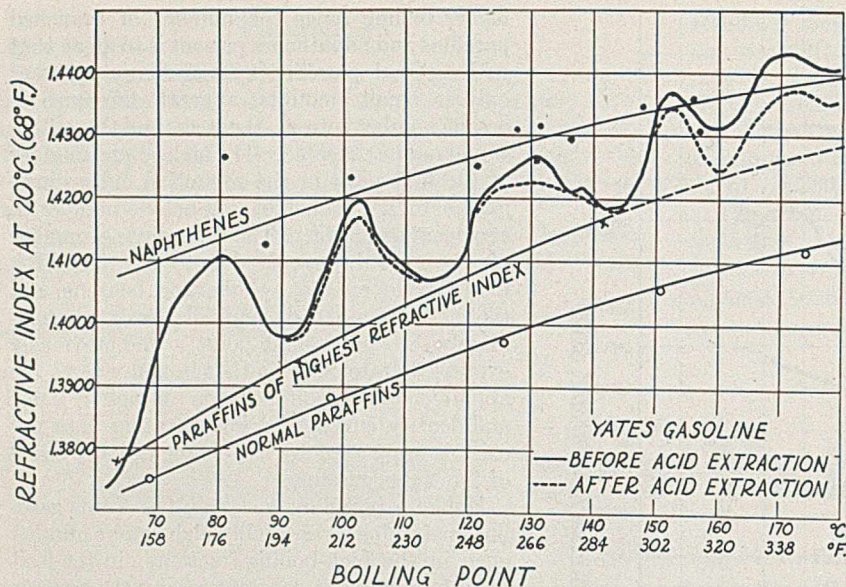


FIGURE 2. REFRACTIVE INDEX BEFORE AND AFTER ACID EXTRACTION

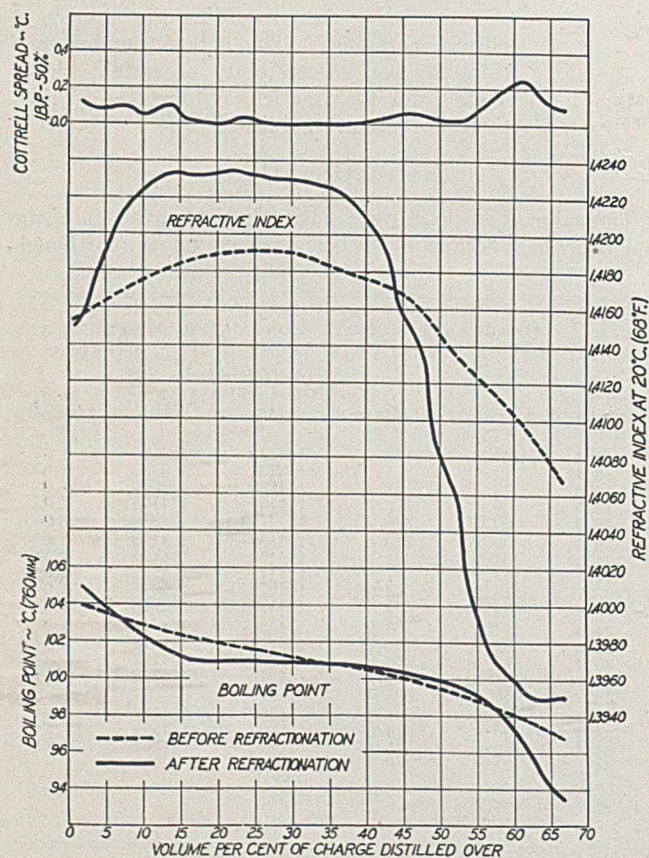


FIGURE 3. REFRACTIONATION OF METHYLCYCLOHEXANE FRACTIONS

the column of seventy-five theoretical plates effects a good separation of the gasoline, it is possible by refractionation in a hundred-theoretical-plate column of smaller diameter to separate further the constituents. This is possible for three reasons: (a) In the original fractionation the column not only has to separate the constituents in question but also to hold back all the higher boiling compounds, (b) the relation of hold-up to concentration of any one constituent is higher in the larger column, and (c) an increase of 25 theoretical plates will considerably increase the degree of separation.

In a paraffinic gasoline the refractionation of a normal paraffin fraction will not radically affect the character of the refractive index curve but will only result in yielding a normal paraffin of greater purity. In a naphthenic gasoline, since naphthenic gasolines appear to be far more complex than paraffinic gasolines, a refractionation may change completely the character of the refractive index and boiling point curves. Although it was obvious that the Yates gasoline was so complex that the isolation of many pure compounds would be difficult and time-consuming, it was considered necessary to prove the absence of normal paraffins and the presence of naphthenes. The normal heptane-methylcyclohexane and normal octane-ethylcyclohexane fractions were chosen for study.

The material from the 45-gallon fractionation in the seventy-five-plate column boiling from 91.8° to 103.1° C. was refractionated in the hundred-plate column previously described and designated as column A (2). The column was operated as a batch-stripping column; i. e., the highest boiling material was obtained as product. The first charge to the still was 2870 cc., and at the proper boiling point an additional 1850 cc. was added making a total charge of 4720 cc. The lowest refractive index fraction added was 1.3980 and the highest 1.4190. The average reflux ratio was 32 to 1. The results are given in Figure 3 and Table IIIA.

TABLE III. REFRACTIONATION OF FRACTIONS

Frac- tion No.	Vol. % of Charge Distilled	B. P. (760 Mm.) ° C.	Refrac- tive Index, $n_D^{20}$	Frac- tion No.	Vol. % of Charge Distilled	B. P. (760 Mm.) ° C.	Refrac- tive Index, $n_D^{20}$
A. Methylcyclohexane Fractions							
2	1.8	104.9	1.4156	29	31.6	...	1.4229
4	4.1	104.2	1.4182	33	38.1	100.9	1.4218
8	8.0	102.7	1.4216	36	42.8	100.4	1.4191
11	11.5	...	1.4229	39	46.0	100.2	1.4150
12	12.5	101.6	1.4230	42	52.6	99.5	1.4053
17	16.5	101.0	1.4232	45	56.0	99.0	1.3981
20	21.0	101.0	1.4235	48	61.8	96.2	1.3952
24	25.4	100.7	1.4233	50	64.4	94.5	1.3949
27	29.0	100.9	1.4230	52	66.8	93.4	1.3950
B. Ethylcyclohexane Fractions							
1	0.4	137.8	1.4241	60	45.5	...	1.4300
7	4.2	137.4	1.4245	61	46.0	132.2	1.4300
10	5.5	137.3	1.4249	70	53.1	131.4	1.4302
13	7.4	137.1	1.4245	74	56.0	131.2	1.4309
16	9.2	136.9	1.4238	77	59.6	130.3	1.4300
22	13.3	136.5	1.4207	82	64.0	128.6	1.4235
28	18.2	135.8	1.4130	88	68.7	126.5	1.4160
31	20.2	135.6	1.4128	91	70.2	125.3	1.4190
34	25.8	134.7	1.4224	97	74.5	124.4	1.4260
43	32.3	134.1	1.4248	100	77.1	123.8	1.4271
46	34.3	134.5	1.4234	106	81.8	123.4	1.4262
49	36.6	133.9	1.4240	112	87.3	121.7	1.4222

The refractionation yielded 13.5 per cent of the charge having both boiling point and refractive index almost identical with pure methylcyclohexane. For further purification, fractions 11 to 29 (comprising 1011 cc.) were fractionated at a reflux ratio of 50 to 1 in a twenty-theoretical-plate column. The distillate from second to last fraction had a constant refractive index of 1.4232, and the residue of 48 cc. had a refractive index of 1.4220. The first fraction of distillate comprising one per cent of the charge had a refractive index of 1.4209. The physical constants of the best samples of methylcyclohexane are compared below with the physical constants given by Hicks-Bruun (3):



	B. P. (760 Mm.) ° C.	$n_D^{20}$	$d_4^{20}$	F. P. ° C.
From Yates gasoline	100.9	1.4232	0.7700	-127.4
Reported by Hicks-Bruun	100.8	1.4234	0.7693	-126.4

The concentration of methylcyclohexane in the original gasoline is estimated to be 0.8 volume per cent. The amount of material boiling at about 98° C., however, was small and had physical constants different from *n*-heptane.

The material from the 45-gallon fractionation in the seventy-five-plate column (boiling from 121.4° to 136.0° C. at 760 mm.) was similarly refractionated in column A. The first charge to the still was 4,100 cc., and at the proper boiling point additional charges of 790, 2,450, and 2,870 cc. were made, making a total charge of 10,210 cc. The average reflux ratio was 33 to 1. The results are given in Figure 4 and Table IIIB.

The refractionation yielded fractions differing markedly from the original ones. A peak in the refractive index curve at 123.8° C. was obtained and was due to a naphthene. The amount of material boiling at about 125° C. was small and had physical properties different from *n*-octane. At 126.3° C. the refractive index reached its lowest point and then rose rapidly to a peak at 131° to 132° C. Certain of these fractions at the peak had physical constants similar to ethylcyclohexane.

Fractions 60 to 77 of the refractionation were combined and fractionated in the twenty-plate glass column previously mentioned. The first fraction comprising 1 per cent of the charge had a refractive index ( $n_D^{20}$ ) of 1.4259, all other distillate fractions had 1.4303, and the residue comprising about 2 per cent of the charge had 1.4315. A comparison of the

physical constants of one of the intermediate fractions and of ethylcyclohexane (5) is as follows:

	B. P. (760 Mm.) ° C.	$n_D^{20}$	$d_4^{20}$	F. P. ° C.
From Yates gasoline	131.5	1.4303	0.7304	-114.4
Reported by Rose (5)	131.5	1.4320	0.7357	-113.0
Synthetic (5)	131.7	1.4330	0.7380	-111.4

The concentration of ethylcyclohexane in the original gasoline is estimated to be 1.0 volume per cent.

After leaving ethylcyclohexane, the refractive index decreased first slowly and then rapidly to 1.4125 at 135.7° C. The break in the boiling point curve at 134.6° C. was due to the addition of another charge. The next rise was to a naphthene peak at 137.2° C. The behavior of the material boiling from 135° to 138° C. was similar to that of the Ponca City gasoline studied on A. P. I. Project No. 6 (9). The material of low refractive index consisted of isononanes, and the material of high refractive index was a naphthene (9). If the refractionation had included the material boiling from 136° to 138° C., the naphthenes and isononanes would have been more completely separated.

TABLE IV. SUMMARY OF HYDROCARBONS IN YATES GASOLINE

Presence Fairly Certain	Presence Suspected	Absence Probable
Cyclopentane	2-Methylpentane	Benzene
Cyclohexane	Methylcyclopentane	<i>n</i> -Heptane
Methylcyclohexane <sup>a</sup>	2-Methylhexane	<i>n</i> -Octane
Toluene	Dimethylcyclohexanes	<i>n</i> -Nonane
Ethylcyclohexane <sup>a</sup>		<i>n</i> -Decane

<sup>a</sup> Identified.

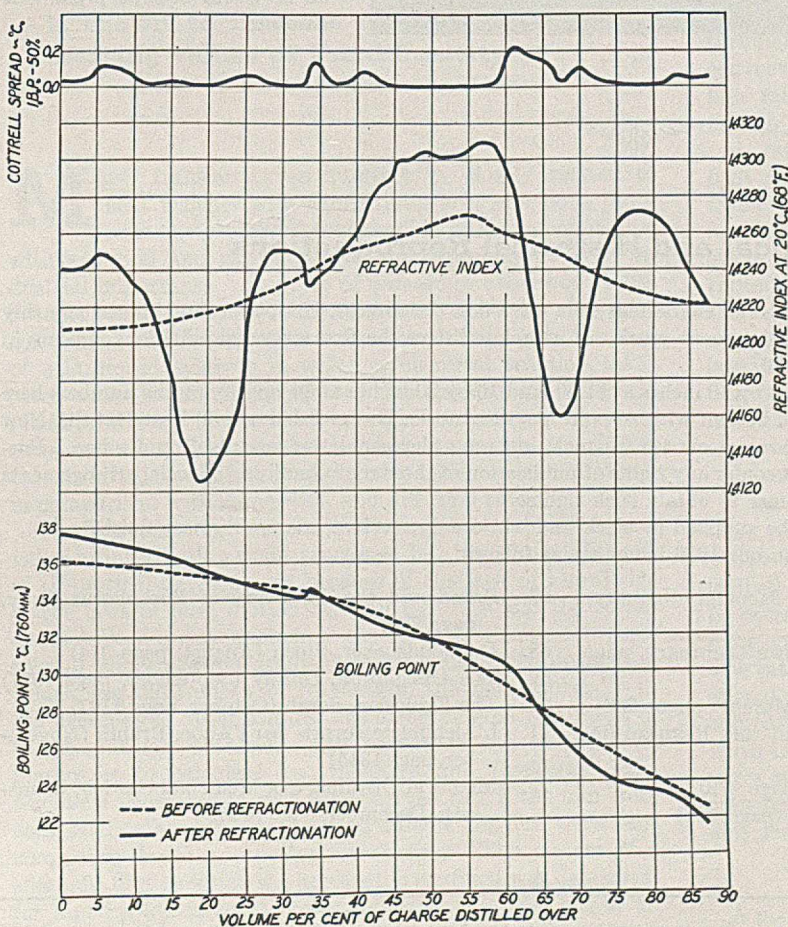


FIGURE 4. REFRACTIONATION OF ETHYLCYCLOHEXANE FRACTIONS

### Acknowledgment

Grateful acknowledgment is due the Shell Petroleum Company for carefully obtaining a representative sample and preparing it for use. In addition, various members of this laboratory rendered valuable help and assistance in the work.

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RECEIVED June 18, 1936.

### Correction

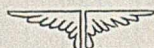
In the "Discussion" by V. B. Browne of the article on "Chromium and Its Alloys" [*IND. ENG. CHEM.*, 28, 1385 (1936)], an error occurs in the first line of the third paragraph. Obviously "12 per cent carbon" should be "0.12 per cent carbon."

## SHOP OF AN ALCHEMIST

By David Teniers, the Elder



● Heretofore we have brought in the Berolzheimer series of Alchemical and Historical Reproductions many of the paintings by David Teniers, the Younger, and expect to publish several more in the future. This month No. 73 in the series, which is ascribed to David Teniers, the Elder, is from the Musée Carcassonne (France). The elder Teniers was born in Antwerp in 1582 and studied under Rubens in Antwerp and Elsheimer in Rome. He achieved his fame largely because of his landscapes, rustic scenes, village life, and the like, although he also painted many religious, mythological, and similar subjects. He died in Antwerp in 1640 after having successfully educated four sons, all of whom became prominent painters.



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| 66. Distillation, Brunswig (June, page 677)                  | 72. Medieval Distilling in a Medicinal Garden, Brunswig (December, page 1445) |

# HEAT TRANSFER AND DIFFUSION RATES AT Solid-Liquid Boundaries

CECIL V. KING AND PAUL L. HOWARD

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Measurements of the rate of heat transfer from a thin platinum wire to rapidly stirred water and sucrose solutions have been made and compared with the dissolution rates of thin copper, zinc, and cadmium wires in aqueous reagents in which the rate is believed to be independent of the chemical reaction velocity.

It is shown that these and other measurements agree reasonably well with some of the requirements of the semi-empirical relations of Chilton and Colburn, which were derived from data for heat and mass transfer processes in gaseous systems. The calculated "effective film thickness" is shown to increase regularly with increasing values of the diffusivity.

**M**ASS transfer at an interface is closely related to heat transfer at a similar interface, and both problems have received considerable study in connection with gas-solid and gas-liquid systems, especially those of industrial importance. In spite of numerous attempts, it has been impossible to disentangle completely the roles played by convection and by diffusion or heat conduction. In the case of solid-liquid systems in which a chemical reaction takes place at the interface, its rate may also enter as another complicating factor; on the other hand, in some dissolution processes, including those used in the present research, the chemical rate is believed to be so rapid that it need not be considered in comparison with convection and diffusion rates.

The film concept of heat and mass transfer has been of great value in interpreting these processes, but has proved difficult of theoretical development because of the lack of knowledge of the laws of fluid motion near an interface and the consequent lack of a clear picture of the layer in which a temperature or concentration gradient exists. Lack of information concerning diffusivities of reagents in solution, especially in the presence of other solutes, has also hindered treatment of the dissolution problem. The best that can be done at present is to calculate an "effective film thickness"—the thickness necessary to give the observed rate if the film were completely stagnant and the fluid outside the film were kept completely homogeneous by the stirring. The picture of a stagnant film to which the gradient is confined was developed for liquid systems by Brunner and Nernst (2, 12) but is inconsistent with present knowledge of hydrodynamics. Prandtl (13) and others, in the heat transfer problem, have

assumed a thin film next to the interface in laminar flow with the temperature gradient extending farther into the turbulent region. Prandtl's relation and a similar one for mass transfer derived by Colburn (5) are developments of the Reynolds analogy between momentum and heat transfer. Both involve the friction factor and a ratio  $u_B/u_m$  of the mean rate of flow at the outer edge of the supposedly laminar layer, to the mean rate of flow of all fluid, both along the main axis of flow. This method of attack avoids the direct introduction of film thickness, but the ratio  $u_B/u_m$  is actually calculated empirically or semi-empirically.

In the case of water in turbulent flow in a tube, Fage and Townend (7) have shown that turbulence persists up to the interface itself. Although flow very near the wall is essentially laminar (but not rectilinear), there is no reason to believe that the  $v$  component of the turbulent motion (normal to the wall) shows a sharp break at any point a short distance from the wall. Rather it shows a regular, though not linear, rise with distance. Only this  $v$  component of turbulence can be effective in the transport of material by convection to and from the surface, and the introduction of flow rates parallel to the surface is necessarily empirical except in so far as the latter may be related to the former.

A rather successful semi-empirical method of predicting heat and mass transfer coefficients has been developed by Colburn (6) and by Chilton and Colburn (4). The experimental rate coefficients,  $h$  and  $k$ , in gas-liquid or gas-solid systems are expressed in terms of dimensionless groups which contain the necessary variables and are simple functions of the Reynolds number. The heat and mass transfer factors are presumably equal to each other and equal or closely related to the friction factor. This treatment avoids the question of film thickness and of any flow rate except the mean rate of all fluid. The factors, in form suitable for use in aqueous solutions, are:

$$j_{\text{heat}} = \frac{h}{cG} \left( \frac{c\mu}{K} \right)^{2/3} \quad j_{\text{mass}} = \frac{k\rho}{G} \left( \frac{\mu}{\rho D} \right)^{2/3}$$

The heat transfer and dissolution rate measurements described in this paper were made with the hope that they could be correlated satisfactorily and that they might throw some light on the general theory of the transfer processes involved. The rate of heat transfer from a thin platinum wire to rapidly stirred water and cane sugar solutions was measured, and for comparison the rate of solution of copper, zinc, and cadmium wires in appropriate aqueous reagents was measured. Thin wires were chosen because of the ease of making the heat transfer measurements; the dissolution rates are considerably less precise than with other experimental arrangements.

## Heat Transfer

A platinum wire 0.0055 cm. in diameter and 50.0 cm. long was mounted on a glass holder in such a way that every part of it was approximately 1 cm. from the surface of a hard rubber stir-

ring cylinder which was 2 cm. in diameter and 8.3 cm. long, and had four grooves ( $2 \times 2$  mm.) cut lengthwise in its surface. The wire and stirrer were surrounded by liquid in a liter beaker.

The wire was heated with an accurately measured current (about 0.5 ampere) from a set of storage cells; its temperature could be determined at any moment with an accuracy of  $\pm 0.02^\circ \text{C}$ . by measuring the potential drop across it. This was done with a Leeds & Northrup type K potentiometer; the resistance of the wire and its temperature coefficient had been measured previously. The temperature of the liquid was read simultaneously on a thermometer, to the same accuracy. From the temperature difference ( $\Delta T$ ), the rate of energy dissipation ( $dQ/dt$ ), and the surface area of the wire ( $A$ ), the thermal transfer coefficient  $h$  was calculated:

$$\frac{dQ}{dt} = hA \Delta T$$

In order to measure the current accurately, the platinum wire was connected in series with a calibrated resistance (17.580 $\Omega$ ) of negligible temperature coefficient. The current through both was determined by measuring the potential drop across this resistance just before throwing the potentiometer across the platinum wire. Since the current fluctuated somewhat, three or more sets of readings were taken for each solution. The temperature difference was usually  $2^\circ$  to  $4^\circ \text{C}$ .; the value of  $h$  does not vary rapidly with temperature or temperature difference. The temperature of the liquid was kept near  $25^\circ$ . Good distilled water and rock-candy sugar solutions were necessary to minimize conduction; they were deaerated to prevent deposition of gas bubbles on the wire.

Table I shows details of the experiments with water. Table II gives average values of  $h$  for water and the sugar solutions and also values of  $K$ ,  $c$ ,  $\rho$ , and  $\mu$ . The values of  $K$ , the thermal conductivity, were obtained by combining the value for water given by Bates (1) with those from the International Critical Tables for sugar solutions.

TABLE I. RATE OF HEAT TRANSFER TO WATER FROM WIRE<sup>a</sup>

Stirring Speed	$E$ across 17.580 $\Omega$	$E$ across Pt Wire	$T$ of Water	$\Delta T$	$dQ/dt$	$h$
R. p. m.	Volts	Volts	$^\circ \text{C}$ .	$^\circ \text{C}$ .	Cal./sec. cm.	Cal./sq. cm. $^\circ \text{C}$ .
2000	8.945	15.354	24.88	3.09	1.868	0.699
	8.948	15.351	24.77	2.98	1.868	0.724
	8.953	15.364	24.80	3.04	1.871	0.711
3000	8.948	15.335	24.64	2.76	1.866	0.780
	8.927	15.303	24.76	2.72	1.858	0.792
	8.918	15.298	24.94	2.77	1.866	0.776
4000	8.955	15.339	24.91	2.30	1.868	0.941
	8.953	15.341	25.01	2.31	1.868	0.936
	8.953	15.340	24.93	2.37	1.868	0.914

<sup>a</sup> Wire 0.0055 cm. in diameter, 50.0 cm. in length, 0.864 sq. cm. in area. R at  $20^\circ \text{C}$ . = 29.484 $\Omega$ , temp. coefficient = 0.0870  $\Omega/^\circ \text{C}$ .

TABLE II. AVERAGE VALUES OF  $h$  FOR WATER AND SUCROSE SOLUTIONS

$C_{\text{sucrose}}, M$	0	0.3	0.6	0.9	1.2	1.5
$K \times 10^5$	143	135	128	121	114	108
$c$	(1)	0.93	0.88	0.83	0.78	0.74
$\rho$	(1)	1.04	1.08	1.12	1.15	1.19
$\mu$	(0.0089)	0.0127	0.0162	0.0234	0.0329	0.0523
Value of $h$ at:						
2000 r. p. m.	0.711	0.692	0.615	0.639	0.544	0.570
3000 r. p. m.	0.783	0.796	0.681	0.731	0.618	0.635
4000 r. p. m.	0.931	0.904	0.839	0.846	0.708	0.723

### Solution Rate Measurements

The zinc, cadmium, and copper wires were mounted on a glass holder similar to that used for the platinum wire and suspended in the same manner in one liter of the appropriate reagent. Dilute acetic and hydrochloric acid solutions containing potassium nitrate as a depolarizer were used with the zinc and cadmium and dilute ferric nitrate with the copper, since the rate is believed to be free from any chemical factor in these reagents (8, 10). After cleaning and weighing (on the microbalance) the wires were immersed in the solution for a suitable length of time, and then washed, dried, and re-

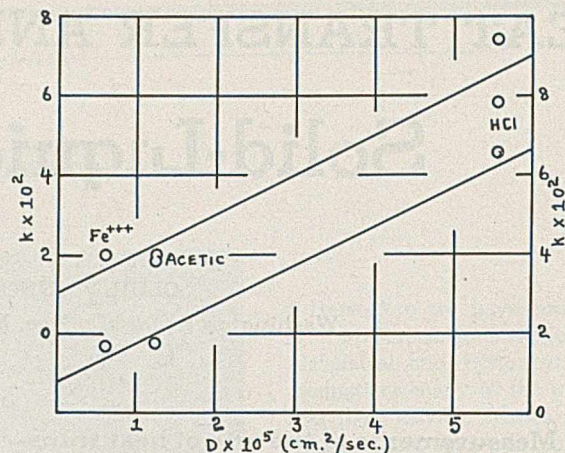


FIGURE 1. DISSOLUTION RATE COEFFICIENTS VS. DIFFUSIVITIES

Lower line (right-hand scale), data at 2000 r. p. m.; upper line (left-hand scale), data at 3000 r. p. m.

weighed. Dissolution rate coefficients  $k$  were calculated from the equation:

$$\frac{dn}{dt} = kAC_{\text{reagent}}$$

where  $dn/dt$  = gram equivalents of metal dissolved per min.  
 $A$  = mean area of wire surface at beginning and end, sq. cm.  
 $C$  = concn. of reagent, gram moles/cc.

Little error is introduced by using the differential form of the equation since only a small fraction of the reagent was used in each experiment.

Theoretically the value of  $k$  should vary with the diameter of wires as thin as these; wires of the same diameter were not available, and the diameter decreased appreciably during the run. No consistent trend of  $k$  with wire diameter was noticed, however, although the rates are decidedly different from those obtained with flat metal surfaces. In comparing the rate coefficients with diffusivities, the greatest error prob-

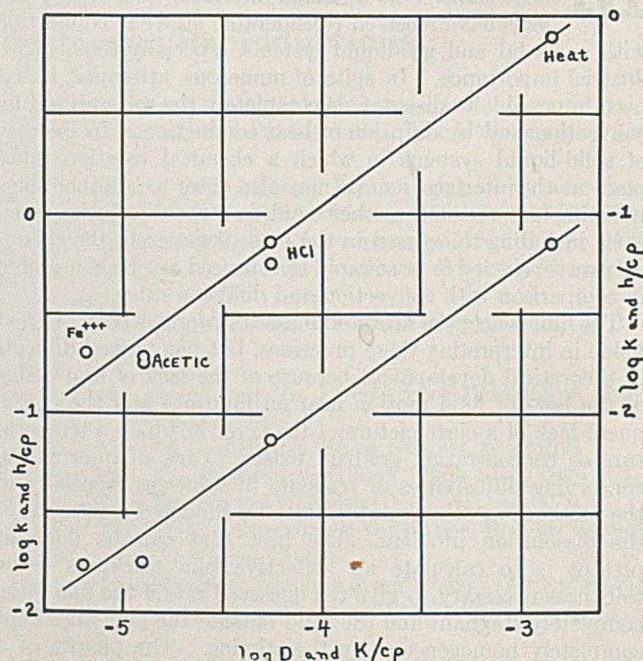


FIGURE 2. DISSOLUTION AND HEAT TRANSFER COEFFICIENTS VS. THERMAL AND REAGENT DIFFUSIVITIES

Lower line (left-hand scale), data at 2000 r. p. m.; upper line (right-hand scale), data at 3000 r. p. m.

ably lies in the difficulty of obtaining measurements under comparable conditions. As shown elsewhere (3, 9), the diffusivities of hydrochloric acid and ferric nitrate are greatly influenced by salts; the best comparison would be obtained by measuring all dissolution rates in salt solutions of such concentration that the reaction products would have little effect on the rates.

Table III summarizes the results of these experiments.

TABLE III. RESULTS OF EXPERIMENTS AT 25° C.

C <sub>reagent</sub> , M	Length Wire, Cm.	Av. Diam., Cm.	Mg. Lost in 5 Min.	$k \times 10^2$		
				3000 r. p. m.	2000 r. p. m.	4000 r. p. m.
Zinc Wire in AcOH; 0.05 M KNO <sub>3</sub> Present; $D_{AcOH} = 1.27 \times 10^{-5}$ Sq. Cm./Sec.						
0.013	52.0	0.02494	9.06	1.74	.....	.....
0.01275	52.0	0.02498	9.00	1.72	.....	.....
0.013	47.4	0.02264	7.87	1.85	.....	.....
0.013	43.8	0.02282	7.83	1.99	.....	.....
Av. 1.83						
Zinc Wire in HCl; 0.05 M KNO <sub>3</sub> Present; $D_{HCl} = 5.56 \times 10^{-5}$ Sq. Cm./Sec.						
0.01155 <sup>a</sup>	52.0	0.02178	24.26	6.04	.....	.....
0.01081 <sup>a</sup>	52.0	0.02214	23.66	6.15	.....	.....
0.01155	52.0	0.02366	25.61	5.85	.....	.....
0.01086	52.0	0.02384	22.02	5.31	.....	.....
0.01155	52.0	0.02456	28.23	6.21	.....	.....
0.01067	53.0	0.02406	23.01	5.49	.....	.....
Av. 5.84						
Cadmium Wire in AcOH; 0.05 M KNO <sub>3</sub> Present						
0.013	29.6	0.00848	3.64 <sup>b</sup>	2.10	1.80	2.01
0.013	33.0	0.00856	3.69 <sup>b</sup>	1.88	1.70	1.85
Av. 1.99 1.75 1.93						
Cadmium Wire in HCl; 0.05 M KNO <sub>3</sub> Present						
0.01155	33.0	0.00826	5.32 <sup>c</sup>	7.55	6.68	8.43
0.01155	33.0	0.00844	6.34 <sup>c</sup>	7.41	6.49	7.89
Av. 7.48 6.59 8.16						
Copper Wire in Fe(NO <sub>3</sub> ) <sub>3</sub> ; $D_{Fe(NO_3)_3} = 0.64 \times 10^{-5}$ Sq. Cm./Sec.						
0.0105	53.6	0.007072	5.06 <sup>d</sup>	2.12	1.77	2.37
0.0105	52.0	0.007124	5.38 <sup>d</sup>	2.31	1.93	2.71
0.0105	53.6	0.006398	1.92 <sup>b</sup>	1.78	1.47	2.22
0.0105	52.0	0.006404	1.88 <sup>b</sup>	1.80	1.62	2.33
Av. 2.00 1.70 2.41						

<sup>a</sup> With 0.3 M KCl added.

<sup>b</sup> In 5 minutes.

<sup>c</sup> In 2.5 minutes.

<sup>d</sup> In 10 minutes.

The diffusivities,  $D$ , given in Table III were selected from measurements by Cathcart (3) as the most probable values for the reagent concentrations used here. The value for hydrochloric acid is the maximum reached in magnesium chloride solutions; that for ferric nitrate, the maximum in potassium chloride solutions. The diffusivity of acetic acid is little changed by salts.

### Discussion

In Figure 1 the dissolution rate coefficients of Table III are plotted against the diffusivities,  $D$ . So far as these and other published (8) and unpublished data obtained in this laboratory are concerned, the values can be represented, within experimental error, by straight lines. These lines do not, however, pass through the origin, as would be required by a constant film thickness, independent of  $D$ ; nor do they pass through the points for the heat transfer coefficients. Two explanations are possible: (1) the extrapolated values of  $k$  at  $D = 0$  are rate coefficients which would be obtained with reagents of zero diffusivity whose transfer to the surface would be by convection alone (this is highly improbable); (2) the points really lie on an exponential curve which is nearly linear over the range of values plotted in Figure 1.

That the rate coefficients, including the heat transfer points, can be represented by a simple exponential relation is shown in Figure 2, where  $k$  and  $h/c\rho$  are plotted on a log-log scale vs.  $D$  and  $K/c\rho$ . The data are reasonably well represented by straight lines with a slope near 0.7. If the

values were plotted, then, against the 0.7 power of  $D$  and  $K/c\rho$ , they would lie on straight lines passing through the origin.<sup>1</sup> This is in accord with the concept of a diffusion layer which increases in thickness with increase in the value of the diffusivity, suggested by King (8) from a consideration of the variation in the  $v$  component of turbulent motion with distance from the interface. It is also in reasonable accord with the Chilton-Colburn relations mentioned earlier, which also require an effective film thickness, increasing with the value of the diffusivity.

The Chilton-Colburn relations may be put in the form,

$$h/c\rho = \alpha(K/c\rho)^{2/3} \text{ and } k = \alpha D^{2/3}$$

where  $\alpha = \frac{jG}{\rho} \left(\frac{\rho}{\mu}\right)^{2/3}$  and is constant at a given flow rate, density, and viscosity.<sup>2</sup>

The exponent  $2/3$  has no theoretical derivation and seems somewhat too low for these and other similar systems. For example, when the rate coefficients of King (8) (obtained from experiments on the dissolution rates of metal and benzoic acid cylinders rotated with a peripheral speed of about 18,400 cm. per minute) are plotted against diffusivities of the reagents on a log-log scale, they lie on a straight line with a slope near 0.8. As shown in Figure 3, the rate coefficients plotted against the 0.83 power of the diffusivities lie on a straight line passing through the origin. This likewise agrees with a film thickness increasing as  $D$  increases.

The decrease in heat transfer coefficients closely parallels the decrease in thermal conductivity of the sucrose solutions. In 1.5 M sucrose,  $h$  is 20 to 23 per cent less than in water,  $K$  is 24 per cent less. The accuracy of the data is insufficient to warrant any further conclusion. This is exactly analogous to the direct proportionality between  $k$  and  $D$  in dissolution rate experiments when the viscosity is increased by adding sucrose (8), and it indicates that the effective film thickness is practically independent of the viscosity. This is probably true, however, only with the type of stirring used here, because of the manner in which the turbulent motion varies with the viscosity at constant stirring speed in revolutions per minute.

The effective film thickness for thin wires can be calculated from the equations:

$$h = K/r \ln \frac{r - x_h}{r}$$

$$k = D/r \ln \frac{r - x_d}{r}$$

The first was deduced by Langmuir for heat transfer from thin wires in gases (11), and the second was similarly derived

<sup>1</sup>  $h/c\rho$  and  $K/c\rho$  have the same dimensions as, and are otherwise comparable with  $k$  and  $D$ , respectively. Since the specific heat and density of all the solutions used, except those containing sucrose, were practically unity, values of  $h$  and  $K$  are actually plotted in Figure 2.

<sup>2</sup> Since for a flat surface  $x_h = K/h$  and  $x_d = D/k$ , it follows that  $x_h = \frac{1}{\alpha} (K/c\rho)^{1/3}$  and  $x_d = \frac{1}{\alpha} (D)^{1/3}$ ; i. e., the effective film thickness should vary with the  $1/3$  power of the diffusivity. The data presented here support this relation if the power is altered slightly.

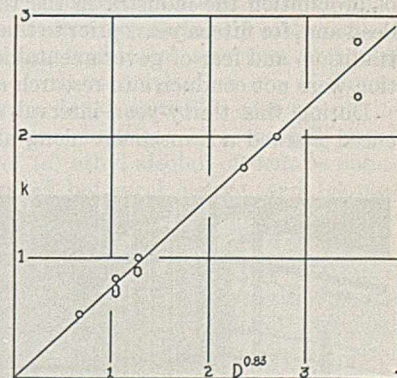


FIGURE 3. DISSOLUTION RATE COEFFICIENTS OF KING (8) vs. 0.83 POWER OF DIFFUSIVITIES

from Fick's law of diffusion applied to this case where  $x_d$  is comparable in magnitude to  $r$ .

The zinc wires used dissolve 2 to 2.5 times as fast, per unit area, as flat disks 1.2 cm. in diameter, having only one face exposed to the solution at the same distance from the stirrer. They also dissolve 20 to 25 per cent faster than metal cylinders of the same diameter as the stirrer and rotating at the same speed.

### Nomenclature

$A$  = surface area of wire, sq. cm. (in Table III, average of initial and final values)  
 $C_{\text{reagent}}, M$  = concn. of reagent, gram moles/liter (unless otherwise noted)  
 $c$  = specific heat, cal./gram, ° C.  
 $D$  = diffusivity of reagent, sq. cm./sec.  
 $G$  = rate of mass flow, grams/sq. cm. sec.  
 $h$  = heat transfer coefficient, cal./sq. cm. sec. ° C.  
 $j$  = Chilton-Colburn heat and mass transfer factors, dimensionless  
 $k$  = dissolution rate coefficient, cm./sec.  
 $K$  = thermal conductivity, cal./cm. sec. ° C.

$r$  = radius of wire, cm. (in Table III, average of initial and final values)  
 $v$  = turbulent motion normal to interface  
 $x_d$  = effective film thickness in dissolution process  
 $x_h$  = effective film thickness in heat transfer  
 $\alpha$  = constant with dimensions of 1/sec.  
 $\rho$  = density, grams/cc.  
 $\mu$  = viscosity, poises

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RECEIVED November 12, 1935.

# Controlling Gin Flavor

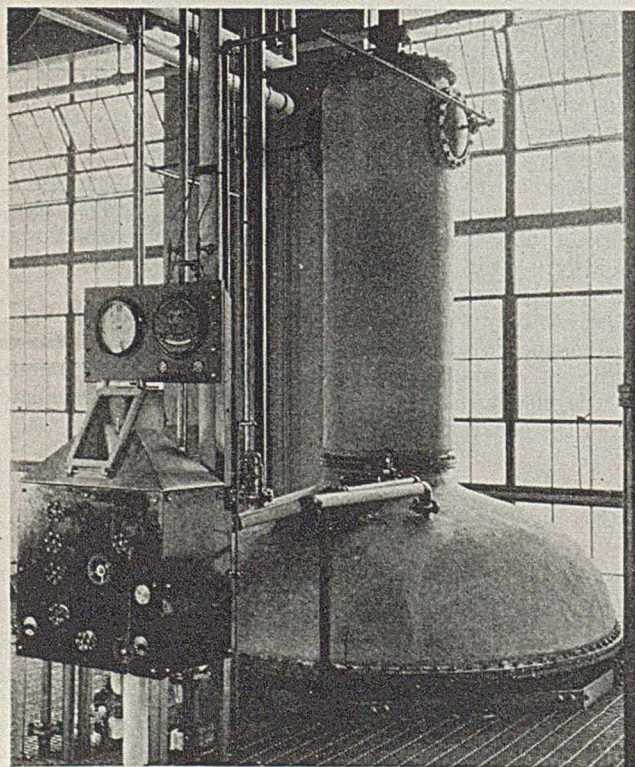
FROM a technical point of view, the beverage alcohol or distilling industry in the United States has been stagnant for at least thirty years. During the years of prohibition the industry in the United States was legally dead and, for fifteen years prior to that time, large inventories, tradition, and fear of governmental interference and prohibition were not conducive to research and development.

During this thirty-year interval other industries experienced marked advancement along all technical lines. Aca-

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Gin production in the past has been characterized by lack of control over many of the important variables such as quality of spirits, quantity and quality of flavor in the various botanicals used, variable types and methods of operating the stills, etc. Critical study of these variables disclosed valuable information which led to standardization of spirits and operations which, with proper selection of botanicals and regulation of the quantity of each ingredient used in the formula in accordance with its flavor value, now permits the production of gin under technical control which guarantees uniformity and quality of final product.



MECHANICAL CONTROLLING AND RECORDING EQUIPMENT  
 ON A GIN STILL

demic and pure research findings had been adopted by the majority of industries, and a technic of industrial research had been developed that had been accepted by practically all plants. This acceptance led to new products, modernization, improvement in quality and uniformity, and greater profits to the management. The liquor industry, which possesses a heritage that dates back beyond recorded history, has always shunned research and development, accepting only those advances that were imperative, such as the classical work of Pasteur, the development of the Coffey still, and a few others. The industry and the consuming public were again robbed of the benefits of industrial, chemical, and biological advances of the age by re-establishing in most plants the old generation of distillers in power following repeal. The industry as a

whole is a paradise for a technical man, but the present management and non-technical-minded operating staffs found in most plants are seriously objecting to the introduction of present-day modern methods of production and control. Since repeal, certain new plants have been built as exact replicas of distilleries of thirty to fifty years ago and are operating without the services of one qualified chemist.

In contrast to these general conditions, with the advent of repeal a few distilleries adopted modern production methods and employed control chemists and chemical engineers; one or two established functioning research departments and placed technical men in operating, control, and administrative positions. It has been the policy of one of these organizations to build upon its 103 years of continuous experience in the distilling industry, to investigate from a modern technical point of view all traditional manufacturing methods and equipment, to replace them, if necessary, with modern methods, and also to remove the black coat of secrecy and empiricism from this business. All engineering, biological, and chemical phases of the operations are under technical control; all have been and are still being studied.

These statements are not intended to be disparaging to others in the distillery business but rather as "food for thought" and encouragement to those who desire to do similar work for this industry, but who, so far, have not been able to convince their management of its merits. The industry as a whole has been inoculated with modern "technical mindedness," and many a chemist awaits with interest the end of the incubation period.

### Periods in Gin Production

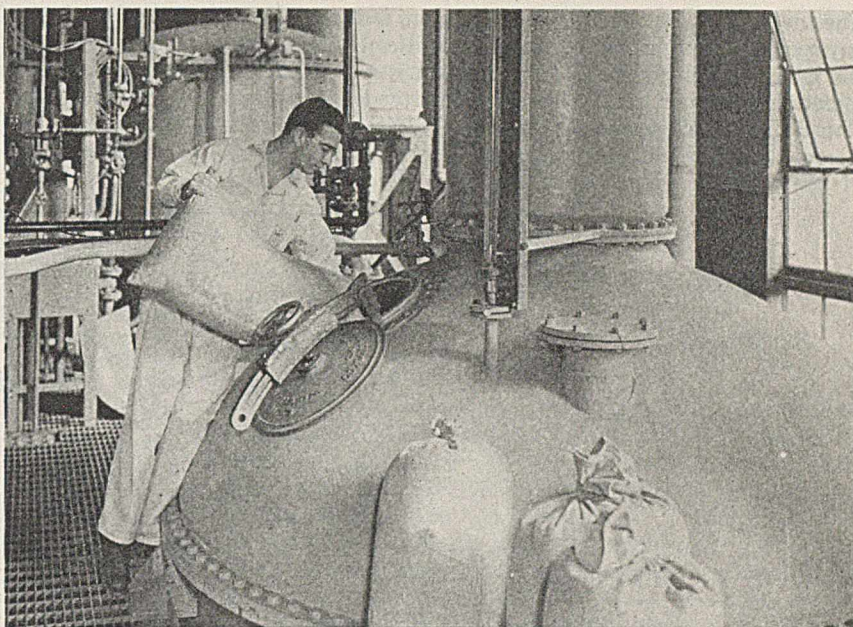
The results of studies on gin production will be discussed, and the manner in which certain medicinal, physiological, chemical, organoleptic, and engineering features enter into its production will be demonstrated.

The production of gin may be said to have passed chronologically through three periods. First came the period of the "coctum," the "philter," and the "pot-stills," dating from the age of its origin in the seventeenth century (26) to the advent of the column still (?). During these years some of the gins must have been fiery potions as a typical formula will show (16):

Corn spirits at proof, gallons	80
Oil of turpentine, pint	1
Culinary salt, pounds	7-8
Water, gallons	30-40
Distill to 100 gallons	

Occasionally "oil of vitrol" (15) was used in place of the salt when a really "hard liquor" was desired. Not even the venerable distillers of Schiedam, Holland, would have described this concoction as a food product.

The second period runs from the beginning of the day of rectification to the present time. Throughout these decades the value of "clean" ethyl alcohol was appreciated and *essence de genièvre* was abandoned in favor of redistillation of ethyl alcohol in contact with or through botanicals. That is, formulas specified a given number of pounds of juniper berries, coriander seeds, cardamom, etc., and, in addition, highly rectified ethyl alcohol (15, 26). This period was also the heyday of secret formulas. Texts, the trade, and the press continue



ADDING BOTANICALS TO A GIN STILL

to display the following type of announcement: "This same renowned secret formula has been in use in our family for decades and has been handed down from generation to generation." An illustrative formula of this period might read as noted in Table II.

The third period which is proposed for adoption by the food and beverage industry is one in which chemistry and chemical engineering take the place of traditional, secretive, and rule-of-thumb methods. The writers propose an era of flavor-controlled gins. Producing flavor-controlled gins orients itself around three primary considerations, all technically regulated—namely, the use of (a) ethyl alcohol of definite specifications, (b) a standardized botanical charge, and (c) mechanically controlled distillation.

### Ethyl Alcohol of Definite Specifications

Today most distillers of gin pay particular attention to the type and kind of alcohol used. The majority of American distillers are using a grain mash as the source of their alcohol for gin. According to Herstein and Gregory (15), objection exists in Europe to the use of molasses alcohol due to its harsh top notes, but apparently this is not so true in America although we must admit that there is some prejudice against the use of anything except grain alcohol. Recently, the question has been raised as to whether synthetic alcohol, now illegal for beverage purposes, might serve as a source of alcohol for gin, etc. The presence or absence of alleged toxic constituents (4, 18, 19, 20, 25) in synthetic ethyl alcohol is still a debated question. It is to be regretted that an editorial (17) and a reliable article appearing recently on this subject (4) carried no claims relative to the therapeutic action of commercial grades of synthetic ethyl alcohol, but reported only upon c. p., or laboratory quality, which they concluded to be comparable in physiological effect to potable grain spirits. Alcohol from grapes is as yet far too expensive to be considered in America for the manufacture of gin.

Alcohol for this purpose must be free from all but traces of odoriferous impurities which occur in minute quantities in the commercial product and owe their source to the raw materials from which they are manufactured (8). Potato alcohol, even though highly rectified, gives a different bouquet from rice alcohol. Likewise, the other commercial grades of alcohol can be identified best by their characteristic bouquet.

The tools for use in the liquor industry are sadly lacking for any specific determination for these impurities; consequently, the indices developed for identifying "pure spirits" are still somewhat relative. It is largely a matter of good taste rather than intelligence that permits the discrimination between these various spirits. However, when the speci-

made of it. In addition to the evaluation of the quantity of oil present, the character or flavor type of the botanical must be controlled by means of specifications. After selection and purchase of the botanicals, they should be warehoused under regulated humidity and temperature conditions to preserve the desired flavorings.

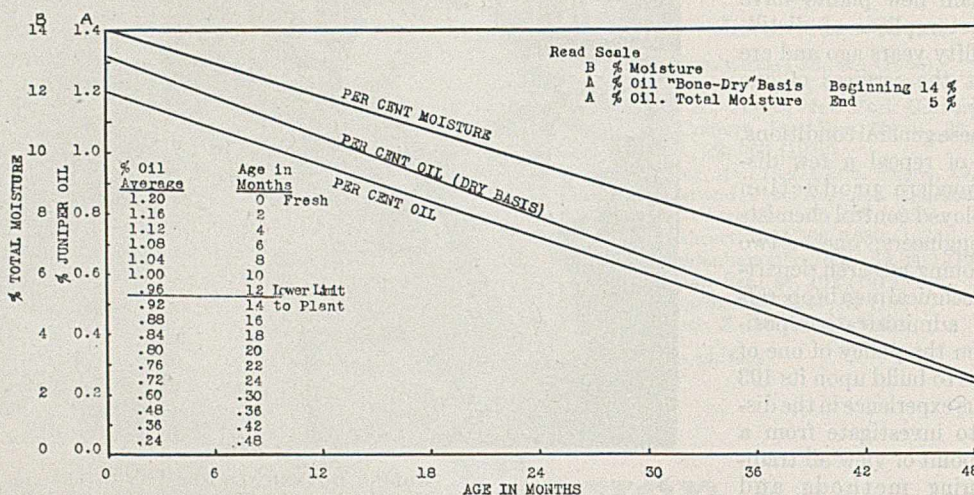


FIGURE 1. LOSS IN VOLATILE OIL OF JUNIPER BERRIES (ITALIAN) WITH AGE BY CLEVENGER METHOD (STEAM DISTILLATION)

cations given in Table I are required, a high grade of "Cologne spirits" suitable for a mild gin, is obtained.

The methods employed in all these determinations except the permanganate time and bouquet are found in the official methods of the A. O. A. C. (2). That for the permanganate time is given by Allen (1), and the technic of bouquet analysis is a tradition of the industry.

A comparative analysis of commercial samples of alcohol from different sources (Table I) indicates how closely grain and molasses alcohols approximate the proposed standards.

### Standardized Botanical Charge

The assay and regulation of the weights of the various ingredients used in accordance with their flavor value is an innovation in the field of liquor manufacture. Whereas in the past all gin formulas read only in terms of pounds of each ingredient per unit quantity of alcohol (Table II), the research department of Hiram Walker & Sons, Inc., and associated companies developed a method of flavor assay and now select their botanical ingredients and modify the poundage formulas in accordance with the flavor value of each ingredient as noted in Table III. Disclosed in this tabulation is the main factor in flavor control. Since the essential oils and associated volatile constituents of the crude drugs communicate the intensity of flavor and character to the gin, in spite of the opinion of one well-known gin manufacturer to the contrary (3), the addition of a regulated quantity of each botanical so as to give the same amount of oil in each batch will help to duplicate the flavors, provided the same type of botanical (same character of oil) is always used. The correct weight of botanical to be used in the charge (column C, Table III) is calculated by dividing the weight of that particular oil noted in the standardized formula (A) by the percentage of oil noted in the botanical (B) and multiplying by 100.

Botanicals from identical sources vary in oil and flavor concentration from year to year. Likewise, they vary in type, quality, and quantity of flavor in accordance with geographical source. Flavor value also changes with unconditioned storage. Thus it is necessary to standardize the herb, berry, or root, as the case may be, before any use is

Since juniper oil is the chief flavoring constituent of all gins, the requirements of their assay will be discussed in detail, dismissing all other botanicals with the summary statement that they are likewise rigorously examined.

It is believed that many of the specifications here disclosed are unique and not to be found in the literature by virtue of the fact that data are ordinarily gathered from freshly harvested products and are not the same as those noted for seasoned (aged) botanicals. Caraway seed, for example, as harvested and distilled in Holland, is reported to yield around 6 per cent oil (12). When what is reported as legitimate Dutch caraway seed arrives in America, weeks distant from the day of gathering, distillers find about 2.5 per cent oil. We may attribute this difference to shipment of "drawn" seeds or to volatilization of part of the oil by aging. At any rate, the recipient of the aged seeds never realizes the same value as was present when the seeds were harvested. This same situation applies to other botanicals (11, 13). Thus a modern gin manufacturer should assay all of his crude drugs.

### Juniper Berries

The following specifications for juniper berries have been developed and found satisfactory by the writers for preparing a uniform high-grade potable gin:

1. Ripe berries of the *Juniperus communis* from the Chianti region of the Apennine Mountains of immediate harvest past; maximum age, one year.
2. Not more than a total of 4 per cent unripe stock, oxycedrus berries, damaged goods, dead berries, and other adulterants shall be present.
3. The moisture content shall not be less than 7 per cent by weight as evaluated by the Dean-tube method at 20° C. on a sample previously dried in a desiccator for 16 hours over 66° Bé. sulfuric acid. The total moisture as determined by the loss in the desiccator and the Dean tube shall not exceed 14 per cent.
4. The acid number shall be 13 to 17 when determined on the fruit as calculated on a 7 per cent moisture basis and no more than 3 when determined on the volatile oil steam distilled therefrom.
5. The per cent volatile oil shall not be more than 1.6 or less than 0.9 when determined by the Hiram Walker method.
6. The per cent volatile oil shall be 0.9 to 1.2 when determined by the Clevenger method.



7. Average size of the berries shall be 8 to 10 mm., and the color shall be steel blue.
8. Average number of berries per gram shall be 8 to 10.
9. Specific gravity of the oil shall be 0.8650 to 0.8792 at 20°/20° C.
10. Refractive index of the oil at 20° C. shall be 1.4840 to 1.4870.
11. One part of oil shall be completely soluble in 5 parts or less of 90 per cent alcohol.
12. The unpurified natural oil is to possess "juniperol" bouquet, not a terebinthinol or turpentine odor.
13. A distillate of an alcoholic infusion of the juniper berries shall possess a type of flavor which checks with standards held in the laboratory files.
14. Juniper berries, when combined with the remaining ingredients called for by the formula and when added in accordance with the oil values established for each ingredient, must give a gin that corresponds with standards held in the laboratory files.

The authors wish to point out that they do not propose these constants as the last word in assay. Experience may show the necessity of modifying some of them and likewise better means of evaluating all. They are serving their purpose very well in standardization and may act as sign posts along the way for others to secure better botanicals.

### Source and Age of Juniper

Through the assistance of others, twenty-five different sources of juniper berries (24) have been brought under this assay. They differed as to type and original geographical origin. Some of the samples were dismissed because of unreliable markets, limited supply, or toxic nature (23). After selection of the types that would bear investigation for flavor values, 10 kg. of each of five geographic kinds were obtained and have been studied week after week for a period of over one year. This study is being continued. When these berries arrived in the United States (not more than 6 months after harvest) the surface moisture, volatile fraction

at 110° C., acid number of the fruit, per cent oil, nonvolatile fraction in the oil at 110° C., Dean-tube moisture, gravity, and refractive index of the oil were measured, and a pilot still distillation was made of each type of berry. Polarimetric measurements were not made because of the large quantity of oil required for this study and the limited amount of samples available. The junipers studied included the following:

Variety of Juniper <sup>a</sup>	Locality of Origin
Tyrolean	Assling Valley at 1300 meters
Yugoslavian No. 4	Region of Maribor
Yugoslavian No. 5	Region of Maribor
Italian	Tuscany
Czechoslovakian	Carpathian Mountains

<sup>a</sup> All berries of October, 1934, harvest.

In addition to these data, nearly five hundred samples have been analyzed during the last two years under their reported definitions of variety and source. These include Russian, Czechoslovakian, Swedish, German, French, Italian, Yugoslavian, and Austrian juniper berries. The Italian berries from the Chianti region gave the best flavor. Those Yugoslavian berries raised along the forty-third parallel of latitude or near Zara are nearly as good. If a sharp-flavored gin is desired, German juniper should be used. Gin producers may prefer different types of finished product; hence many differ not only as to the formula but also as to the source and desired age of the juniper. Some distillers prefer to use juniper berries two or three years old. Later the writers will show (in connection with the oil content) specific reasons why they have no interest in two-, three-, or four-year-old berries. A year-old berry is one that has matured one year after the date of harvest. Granted that geographical source and age have much to do with the type, quality, and quantity of flavor found in juniper berries, it becomes necessary for each gin producer to have definite source and age specifications for his berries if he is to produce a uniform product.

### Adulterants

These studies have shown that such specifications are necessary because of the flagrant adulteration so prevalent in botanicals shipped into the United States and subsequently dispensed to the commercial trade. Juniper may be found on the market today with as high as 40 per cent of unripe fruit, oxycedrus, or other contaminants that are harmful to good flavors.

Another reason for care in eliminating the unripe or adulterating berries is shown by the effect of various quantities of these materials on certain physical constants:

	25% Adulteration	4% Adulteration
Austrian berries:		
Per cent oil	1.80	1.20
Refractive index	1.4817	1.4780
Acid No.	21.27	16.65
	38% Adulteration	4% Adulteration
Italian berries, acid No.	19.26	13.89

TABLE I. SPECIFICATIONS FOR AND ANALYSIS OF COMMERCIAL GRADES OF ALCOHOL

Source	Specifications	—Analysis of Commercial Alcohol—			
		Grain	Molasses	Ethylene	Wine
Proof at 60° F. (15.6° C.)	190-192	192.0	190.0	190.5	183.5
Bouquet	Neutral	Neutral	Neutral	Objection- able	Fruity
KMnO <sub>4</sub> time, min.	60 or greater	65	60	40	20
Grams per 100 Liters at 100 Proof					
Aldehyde as AcH	<2.0	1.2	1.5	2.0	5.7
Esters as Et acetate	<7.0	3.7	2.6	3.2	45.0
Acids as acetic	<1.2	0.6	0.9	1.4	0.9
Fusel oil as amyl alcohol	<7.0	6.0	9.0	4.7	18.6
Extract	<0.7	0.5	0.8	0.6	1.0

TABLE II. STANDARD TYPE OF GIN FORMULA<sup>a</sup>

(In pounds per charge of 3000 wine gallons at 100 proof)			
Ingredient	Pounds	Ingredient	Pounds
Juniper berries	100	Angelica root	10
Coriander seed	50	Lemon peel	1
Cinnamon bark	10	Cardamom	1

<sup>a</sup> This formula is used purely for illustrative purpose and does not represent a true potable gin production formula.

TABLE III. FLAVOR-CONTROLLED GIN FORMULA<sup>a</sup>

(In pounds per charge of 3000 wine gallons at 100 proof)							
Code No.	Ingredient <sup>a</sup>	Type	Source	Date of Purchase	A	B	C
					Lb. of Volatile Oil in Standard Charge	Volatile Oil in Botanical, %	Lb. of Ingredient per Charge
520	Juniper berries	Italian	W-1	5/4/36	1.0	1.2	83.3
521	Coriander seed	Moroccan	K-1	6/10/36	0.5	1.0	50.0
522	Cinnamon bark	Ceylon	K-1	7/1/36	0.15	1.5	10.0
523	Angelica root	Saxonian	C-3	8/15/35	0.15	1.0	15.0
524	Lemon peel	Sicilian	C-3	6/16/36	0.001	0.2	0.5
525	Cardamom	Mysore	C-3	7/7/36	0.02	2.0	1.0

<sup>a</sup> This formula is used purely for illustrative purpose and does not represent a true potable gin production formula.

Since we wish to rely upon a certain range in chemical and physical factors for flavor control, obviously these constants must be fixed. Unripe and oxycedrus berries are a beautiful rich brown, whereas the communis berry is gun metal or midnight blue. Hand-selected berries are chosen now by some discriminating distillers.

### Moisture Content

Obviously, unless the distiller is to consider water as a variable in his scheme of assay, he must select berries of the same range of moisture

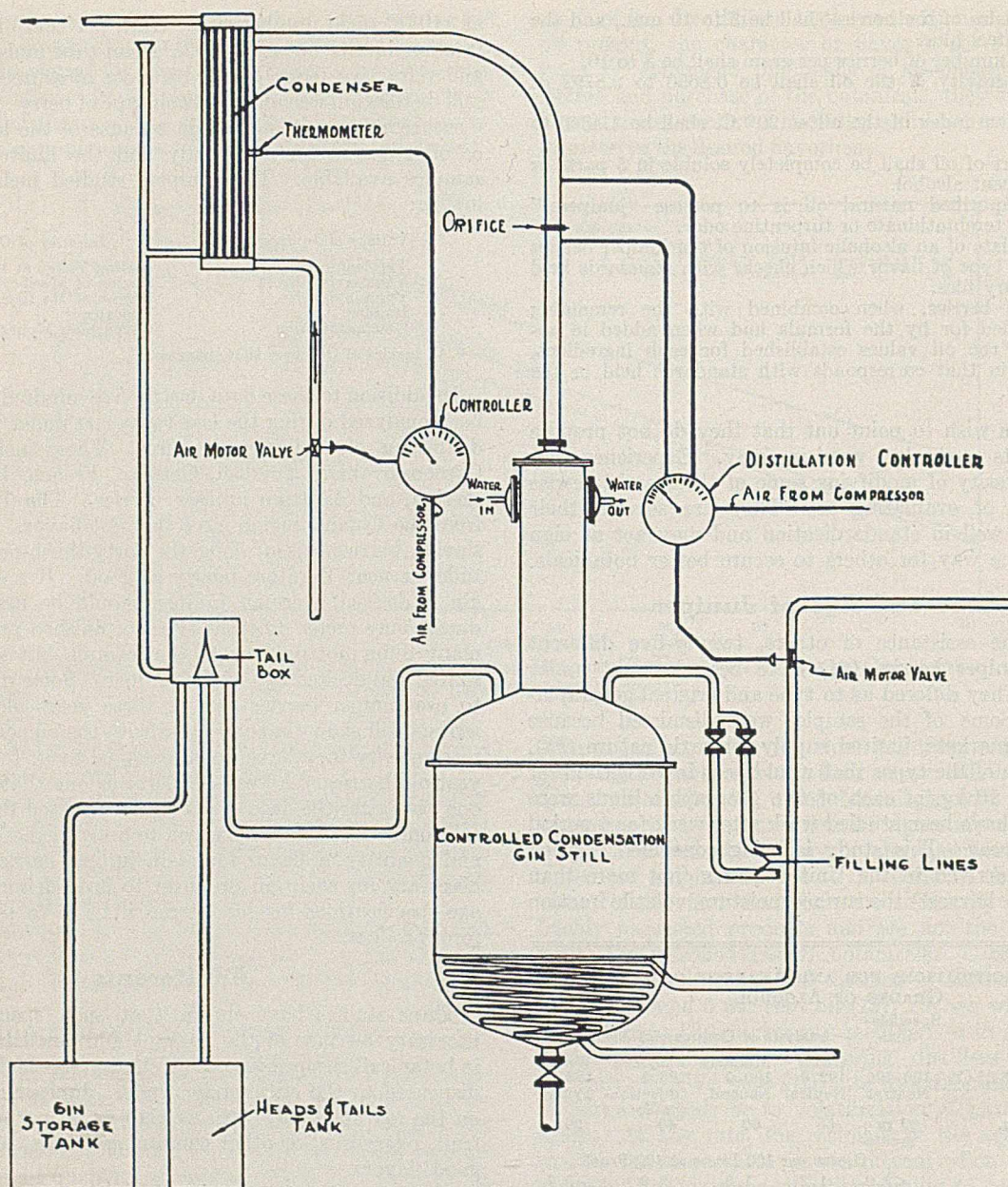


FIGURE 2. CONTROLLED CONDENSATION GIN EQUIPMENT

content, both as regards surface moisture (water lost on drying in a desiccator) and Dean-tube moisture. Very dry berries are synonymous with very old berries.

Popov and Pashkevich (21) claim that the maximum total moisture content of freshly harvested juniper berries should not be over 16 per cent and that 12 per cent is about normal. Several types of juniper berries were received with a maximum age of 8 and a minimum of 6 months. These berries were warehoused under uncontrolled conditions for 12 months, and the moisture content was measured weekly. The data obtained indicate that humidity, storage temperature, and the surface texture of the berry affect moisture values. The maxima and minima data for the several types examined are as follows:

Type	% Moisture by Weight <sup>a</sup>		
	6 mo.	12 mo.	18 mo.
Tyrolean	8.6	6.6	4.5
Czechoslovakian	9.3	6.5	4.1
Italian	8.8	7.2	5.6
Yugoslavian No. 4	10.1	6.4	4.7
Yugoslavian No. 5	10.1	8.2	4.5

<sup>a</sup> Moisture content by Dean-tube method after drying 16 hours over 66° B<sub>e</sub>. H<sub>2</sub>SO<sub>4</sub> to eliminate surface moisture.

Numerous analyses and data collected on 100,000 pounds of plant stock conclusively demonstrate that a minimum moisture content of 7 per cent is justifiable for an Italian berry not more than 12 months old.

The above figures and Figure 1 indicate loss in moisture noted in berries stored in an unconditioned warehouse for various lengths of time. Temperature- and humidity-controlled warehousing should reduce loss in moisture and retard oil and flavor losses. There is also a practical side of this question—namely, that the drying of the berries with the attendant loss in oil (Figure 1) is a total loss in investment at the rate of the cost of the berries, which runs from 5 to 9 cents per pound. This loss may amount to 20 to 33 per cent for undried berries held 52 weeks in unconditioned warehouses:

Type	Original Total Moisture, %	Loss in Total Weight, %
Tyrolean	12.98	29.4
Czechoslovakian	15.14	21.9
Italian	15.11	20.0
Yugoslavian No. 4	17.51	32.7
Yugoslavian No. 5	14.00	19.5

Economical and flavor control data, therefore, justify the fixing of specification 3.

### Acid Number

Naturally when the distiller seeks a beverage that is mild and bland in taste he wishes to eliminate those tones responsible for the rasping top notes in bouquet and the astringent character. This is best done by selection of berries or herbs low in terpenic constituents and low in acid number. A low acid number is not always the entire story. Along the forty-third and forty-fourth parallels of latitude in Yugoslavia and Italy grow very good junipers of the communis variety. Northward near the forty-sixth parallel to the Assling Valley, Tyrolean berries are found. Still farther north, the German and far to the west in the tradition-infested Carpathian Mountains, the Roumanian, Polish, and Czechoslovakian berries are found. The Tyrolean berries are easily differentiated from these others because of their high acid number:

Type	Age	Acid Number <sup>a</sup>		Av.
		Minimum	Maximum	
Tyrolean	6-18 mo.	17.6	19.0	18.3
Czechoslovakian	6-18 mo.	14.8	16.3	15.5
Italian	6-18 mo.	14.9	16.7	15.8
Yugoslavian Nos. 4 and 5	6-18 mo.	13.5	15.8	14.7
German	1-3 yr.	10.0	13.0	..
American	Fresh	6.0	8.0	..
Russian	1-3 yr.	2.0	4.0	..

<sup>a</sup> Calculated to 7.0% moisture basis.

However, acid number is not the entire answer to good flavor; for, although Czechoslovakian berries lie within the range of the Yugoslavian and Italian, and data from a number of shipments indicate that German berries give acid numbers ranging from 10 to 13 (average near 12), American 6 to 8, and Russian even as low as 2 to 4, the flavor of these berries is much less sweet than that of the Italian. Obviously, then, the botanical to be used cannot be selected by one single specification; for example, berries of the juniper variety raised much above the forty-fifth parallel, even though high or low in acid number, are terebinthinate and pinene-like. Moreover, in southern France along the desirable forty-third and forty-fourth parallels where the thurifera grows, these products are reported as toxic (22). The inclusion of the acid number of the oil is for the purpose of satisfying U. S. P. requirements (acid number less than 3).

Data indicate that the acid number of the fruit may be considered for all practical purposes to remain unchanged during one year of storage, but that of the volatile oil increases. All acid numbers were determined according to the U. S. P. definition—milligrams of potassium hydroxide needed to neutralize 1 gram of berries. Selection is made from a composite sample of one hundred bags. One-fourth pound (113 grams) is dried over concentrated sulfuric acid and ground, and 2 grams are selected for analysis. This sample is covered with 25 cc. of 190-proof alcohol, allowed to infuse 16 hours, and filtered, and the residue is washed with 25 cc. of alcohol. The alcoholic washings are titrated with 0.05 N potassium hydroxide using phenolphthalein as an indicator.

Allowing for a reduction to 7 per cent moisture, the acid number limits have been fixed at 13 to 17 in order to include both Italian and Yugoslavian and to exclude Tyrolean, German, and American berries. Some distillers would like to shift these figures in order to include German berries.

### Volatile Oil

From oil analyses (Clevenger method, 5) on old and new stocks of berries held in warehouses and the reported data on the distillation of fresh berries in Europe, an aging curve has been constructed. This is shown as a "best straight line" in Figure 1. This stock had an initial average total

moisture content of 14 per cent which decreased to 5 during 48 months of unconditioned storage. Likewise, the oil content decreased from 1.3 per cent on a dry basis to 0.25.

The observed oil values on a number of types of juniper over a 52-week storage period (from 6 to 18 months in age) are as follows:

Type	Per Cent Oil		
	Maxima	Minima	Variation
Tyrolean	2.45	1.17	1.28
Czechoslovakian	1.58	0.96	0.62
Italian	1.83	1.55	0.28
Yugoslavian No. 4	1.58	1.18	0.40
Yugoslavian No. 5	1.75	1.04	0.71

These values were determined by a method employed in the Hiram Walker laboratories. This technic is, briefly, as follows: The method involves extracting the crude drug by ether and evaporating the solvent at 47° C. That portion of the residue volatile at 110° C. and by steam is calculated as essential oil. There was less loss of oil from the Italian than any of the other berries. These oil data also indicate the error in using a definite poundage of a botanical for a unit quantity of alcohol. For example, 100 pounds of Tyrolean berries might have charged 2.45 pounds of oil or 1.17 pounds of oil, depending upon the age of berry (6 or 18 months), weather, temperatures, and possibly storage conditions. The weight of botanicals used for gin charges must be regulated as shown in Table III.

Oil values on fresh berries from various sources are as follows:

Origin	Volatile Oil Content, %	
	Steam distn.	Walker method
American	.....	3.0-4.0
Italian	1.2-1.1	1.8-1.6
Yugoslavian	1.1-1.0	1.6-1.2
French	0.6-0.9 (β)	.....
Swedish and Finnish	0.5 (β)	.....
Russian	4.0-5.0 (β)	1.0-1.9
German (Thuringian)	0.6-0.9 (β)	1.3-1.0
Polish	0.6-0.9 (β)	1.6-1.2
German (West Prussian)	0.6 (β)	.....

Studies indicate that unripe berries give high oil percentages. American juniper from the Rocky Mountains contains as much as 3 to 4 per cent oil, but it is quite turpentine-like in character. Thus, by assay limits on oil analysis, we may exclude many undesirable types of berries as well as old ones.

The foregoing studies, in addition to the fact that the writers prefer Italian or Yugoslavian berries, led to the specifications for volatile oils.

### Refractive Index

The refractive index of authentic samples of juniper oil are as follows:

Source of Berries	Hiram Walker Lab.	Guenther (14)	Gildemeister
	(Berries 6 to 12 Mo. Old)	(Fresh Berries)	and Hoffmann (9) (Fresh Berries)
Tyrolean	1.4791-1.4816	1.4756-1.4817	.....
Czechoslovakian	1.4790-1.4825	1.4795-1.4818	.....
Italian	1.4812-1.4870	1.4790-1.4842	1.4790-1.4840
Yugoslavian No. 4	1.4817-1.4841	.....	.....
Yugoslavian No. 5	1.4817-1.4837	.....	.....

The Hiram Walker research department selected a refractive index of 1.4840 to 1.4870 as giving a mild, sweet type of juniper flavor. These values are conditioned by the technic of distillation. It is interesting to note that this value serves to exclude the undesirable Czechoslovakian berries and also those from the Tyrol. Age is believed to enhance this index. This enhanced value may be an indication of deterpenification, a desirable quality. Since terpenes are the most volatile fractions of the oils, they escape first. Pine oils have a refractive index of 1.480 or lower, and a sample of terpeneless juniper in the writers' stock has a refractive index of 1.499. Therefore we may accept a certain rise in this value as a good index, whereas too high a value may indicate very old berries.

### Solubility in Alcohol

Even though alcoholic solubility aids in differentiating old and new stocks and in differentiating one type from another (9, 13), more emphasis is placed upon alcoholic distillation for the selection of the desired berries.

### Bouquet

To date, the writers have not felt it practical to make the isolation or determination of the percentage of any particular terpenic derivative found in juniper oil (such as alpha-pinene, camphene, borneol, isborneol, 4-terpineol, or cadinene) the reason for discarding certain junipers, but they are well aware of the possibilities and are conducting studies on the subject. Oil from *Juniperus phoenicia* L., one of the common species used to adulterate the communis, contains about 90 per cent terpenes, of which the bulk is alpha-pinene (10). The boiling point of alpha-pinene is 156.2° C. The fractional distillations reported on genuine *Juniperus communis* (13) yield only 1 to 2 per cent of the total distillate boiling below 156° C.

To eliminate all possibility of chance, an individual alcohol distillate of the juniper berries should be made in a laboratory pilot still. This should be followed by preparing a complete flavor-controlled gin in the same still. Seldom do constants on the raw stocks fail to eliminate undesirable botanicals. The bouquet of the pilot-still distillates should check with standards that the distiller has collected and preserved in his files.

The physical constants of oils may be adjusted by adding adulterants, but it is very difficult to adjust several constants of the berries.

Numerical analytical values are also important in case a shipment is rejected, since it becomes possible to offer evidence other than organoleptic properties, as to the authenticity of the crude drugs.

### Controlled Condensation

To obviate cutting heads (removal of low boilers) and to secure a continuously identical series of gin distillations, the writers have installed mechanical devices on the gin still to control the temperature of the vapors in the condenser and thus permit the venting to waste from the still of all low-boiling aldehydes and terpenic products derived from the alcohol and botanicals. This method gives the advantage of controlled temperature of condensation. In this operation also, the oils interact with the alcohol and with themselves to produce desirable flavors not secured by cold compounding or, in other words, in "compounded gins." Likewise, automatic control of the quantity of reflux and rate of distillation adds smoothness and uniformity to the final product. This makes it possible to establish, through automatic steam controllers, the exact optimum time and rate of distillation. Figure 2 shows the general scheme of these two automatic controls.

### Heads and Tails

The return of the heads and tails is deleterious to flavor control. Recycling of these fractions permits an accumulation of acid constituents and astringent notes. If the heads

and tails are drawn, they should be cleaned by rectification, thus permitting the re-use of the recovered alcohol.

Obviously the temperature, at which the collection of potable gin is stopped and the tails are sent to a separate tank, is highly important. By varying the cutting temperature, the quantity of the higher boiling fractions of the volatile oils is modified, and hence the taste and bouquet of the gin are changed. Therefore cutting temperatures must also be fixed.

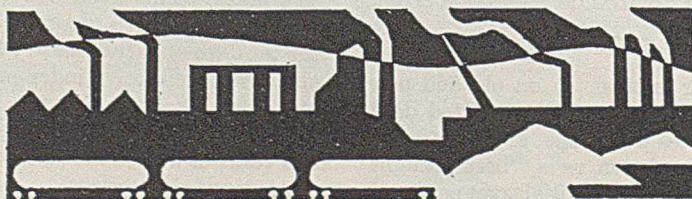
### Acknowledgment

The authors are glad to acknowledge the assistance of Ernest Guenther, chief research chemist of Fritzsche Brothers, in securing legitimate specimens of the botanicals for these investigations; also the assistance of Paul J. Kolachov of the Hiram Walker research staff, who collected many of the analytical data on the authentic samples; and of C. H. Rodgers, chief operating engineer for Hiram Walker & Sons, Inc., for the technic of controlling the rate of distillation and temperature of condensation.

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RECEIVED September 4, 1936. Presented as part of the joint Symposium on Food Processing and Preservation before the Divisions of Agricultural and Food Chemistry and of Biological Chemistry at the 92nd Meeting of the American Chemical Society, Pittsburgh, Pa., September 7 to 11, 1936.

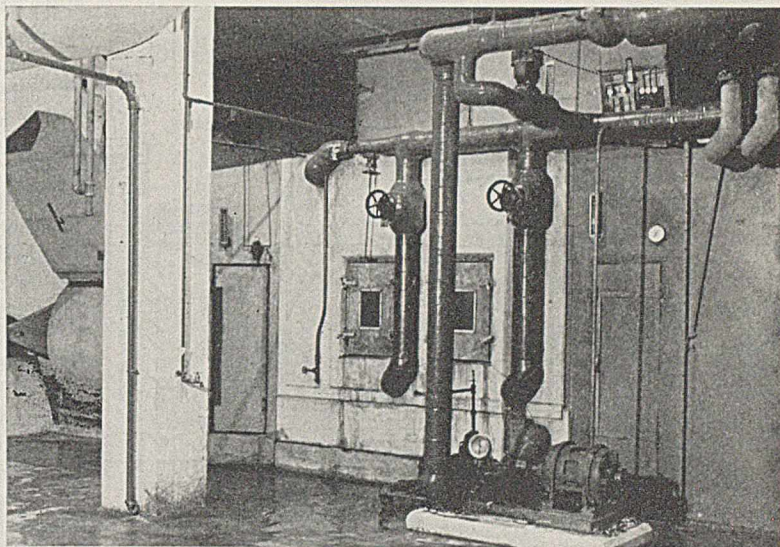


# Bacterial Control in Air Conditioning

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Washing air with sprays of water effects only a partial reduction in the bacterial content. The bacteria tend to accumulate in the washing water and, as the bacterial content of this water increases, the efficiency of bacterial removal from the air decreases. The addition of benzylphenol to the washing water greatly increases the efficiency of bacterial removal; when sufficient benzylphenol concentration is maintained, the water is essentially sterilized. In some cases the bacterial content of the air washed by water so treated is less than one-sixth that of air washed by untreated water.



GENERAL VIEW OF AIR-CONDITIONING UNIT

**T**HE question of the part played by the air in the dissemination of bacterial disease has long been of interest, and the rapidly increasing application of air conditioning to public and semi-public buildings has focused attention upon this problem. The modern air-washing and recirculating systems offer an excellent opportunity for bacterial purification of the air as well as purification in respect to dusts and pollens. It is the purpose of this paper to describe a simple method by which the bacterial content of recirculated air may be markedly diminished.

## Review of Previous Work

The presence of bacteria in air has not been disputed since the time of Pasteur. Flüge and his students demonstrated that virulent tubercle bacilli could be isolated from droplets expelled into the air by persons afflicted with the disease. Winslow (24) showed that the bacterial content of air from different sources varied, and that only a small portion of the bacteria present was of pathogenic significance. Winslow and Robinson (26) concluded, after careful experimental work with *B. prodigiosus* as a test organism, that danger of infection was confined to a local discharge of spray close to the mouth; they regarded ingestion, rather than inhalation, as the principal channel of infection. They claimed that droplets of infective material expelled from a diseased person are ef-

fective only for a few feet, and that they soon fall to the ground. This conclusion was substantiated by others and widely accepted (9, 10, 24).

Recent studies by Wells (17, 19, 21) and his co-workers at Harvard, under conditions which lend more confidence to the results, led to the opposite conclusion. They showed that bacteria contained in minute liquid droplets, expelled into the air and rapidly evaporated, are present in a fine smoke-like form and do not settle, but may drift for hours on currents of air. They were able to recover *Pneumococcus* type I, *B. diphtheria*, *Streptococcus hemolyticus*, and *Streptococcus viridans* from the air of a still chamber 48 hours after artificial inoculation. They also showed that large numbers of typical nasopharyngeal organisms are projected into the air by sneezing and can be recovered from the air in appreciable numbers 10 minutes after the room has been vacated. Wells estimates that an average of more than 20,000 of these organisms are thrown into the air with each sneeze. By mathematical considerations, Wells shows that if an infective droplet expelled by coughing or sneezing possesses an initial diameter less than 0.1 mm., it will evaporate completely before reaching the ground (6 feet), and the bacteria will remain in the air as "droplet nuclei."

The work of Wells seems to prove conclusively that pathogenic bacteria can remain suspended in air and viable for long periods, and that they can be widely disseminated by air currents. This in no way implies that disease may be spread in this manner, since no evidence of epidemiological significance has as yet been presented to show that such contact with infectious organisms by normal persons will cause the corresponding malady. Nevertheless, it would seem to be good practice to maintain the air circulated in any ventilating system as nearly sterile as possible. As Wells states (19): "Reasonable efforts to free air supplies from living microorganisms are justified in the light of general sanitary principles, and should not have to wait demonstration that nasopharyngeal infections can be reduced by sanitary air control to a degree comparable to the reduction of intestinal disease by pure water supply."

It is frequently assumed that the water scrubbing, to which the circulating air is subjected in the average humidifier, will effect the removal of bacteria, as well as dusts, molds, and pollens, with a high order of efficiency. Actually however, there is much evidence to the contrary. Although it is fairly well agreed that dusts and pollens are removed by air washers, the Whipples (22) are apparently the only investi-

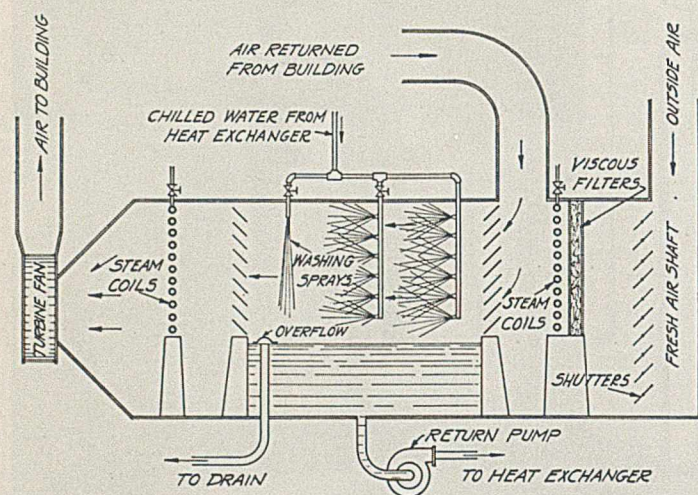


FIGURE 1.  
AIR-CONDITIONING UNIT

gators on record who found a reduction in bacteria. In a study of several systems in Boston and Springfield, they found that washing the air reduced the bacterial content by 0 to 100 per cent, the results varying widely. Dust was reduced by 5 to 64 per cent. Both dust and bacteria were found to concentrate in the washing water.

In direct opposition to these results is the work of Larson (11), who investigated the efficiency of the air-washing system in a Minnesota school building. Larson found that "when using recirculated water, the washer supplied bacteria to the air instead of removing them, and even when using new water continuously, it did not show any marked efficiency as a bacteria remover." An analysis of his tests shows that the bacterial content of the washer water increased logarithmically when the water was recirculated over a 5-day period. That this rate of increase is not due merely to concentration of the water is shown by the fact that the increase in total solids occurs at a linear rate. Clark and Gage (5) showed that the use of air washer water polluted with *B. coli* resulted in an increase of the number of these organisms in the humidified air of textile mills.

Wells (14) showed that in air-washing systems using polluted water, the bacteria of the water were thrown into the air and could be recovered from distant parts of the building. In some cases, most of the bacteria present in humidified air were introduced from the humidifying water.

Since Larson's work shows that pure water soon becomes highly contaminated when used for air washing, the water in any humidifier or air washer may be regarded as polluted, and it is probable that no air washer possesses much lasting value from the standpoint of bacterial removal.

Air filters are probably not much more efficient than air washers. According to Drinker and Wells (7), "no commercial filters which attain high bacterial filtering efficiency in terms of the (Drinker and Wells) test methods are known."

Aside from purely bacteriological considerations, there are varying viewpoints concerning the effects of air conditioning upon health which may be related to infectious bacteria in some manner. Thus Rowe (15) claims that air conditioning

reduces the incidence of various respiratory infections. Yaglou, Drinker, and Blackfan (27) report a case in which the application of complete air conditioning to a premature-infant nursery reduced infection and mortality, the latter by 50 per cent. On the other hand, McConnell (13) claims that "convincing evidence has not been collected which demonstrates a diminished incidence of respiratory or other illnesses among groups of workers who are exposed to conditioned air for 7 or 8 hours during the working day as compared to similar groups not so exposed but working under conditions which may be considered fairly good from a ventilation standpoint."

There has been some interest in various means of rendering the air in circulating systems sterile from a bacteriological standpoint (2, 6, 12). Most of the methods proposed cannot be applied practically to the usual type of air-conditioning system. Cambier (4) found ultraviolet light very effective in eliminating bacteria from the air, and Wells (19, 20) has recently advocated essentially the same process.

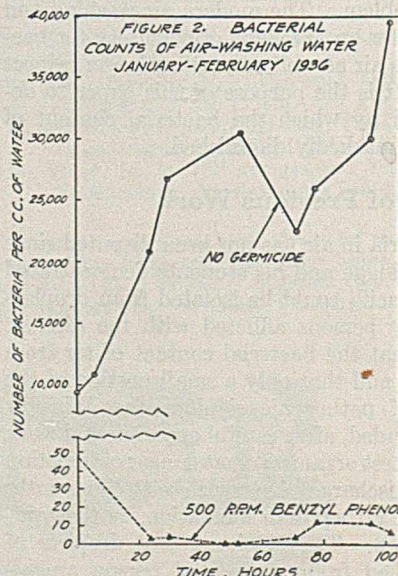
This report describes the use of a germicide in the air-washing water, a technic which possesses many advantages from the standpoint of cost and convenience.

Most of the common antiseptics, such as chlorine, chloramine, phenol, cresols, and the chlorinated phenols, cannot be used because of the odor imparted to the air. Since the amount of air in contact with the water is relatively enormous, a substance of distinctive odor may seriously taint the air, even though its vapor pressure is quite low. Mercurials and copper salts cannot be used since they are extremely corrosive to the metals which make up the equipment. Ammonium salts and amines cause corrosion of copper and brass parts.

The ideal germicide for bacterial control in air conditioning should be highly toxic to the organisms involved, noncorrosive to the metals usually used in engineering equipment, odorless when used in effective concentration, nonvolatile, nontoxic to man and to higher animals, economical and safe to use, stable even on prolonged aeration, and easily dissolved in water. A commercial mixture of the *o*- and *p*-benzylphenols meets these requirements and was therefore selected for use in this work. These benzylphenols are not only effective in high dilution against many types of bacteria but have the added advantage of being particularly toxic to algae and protozoa, and hence are well adapted to slime control. Although slime control is not directly related to the problem

of bacterial reduction in the air, it should be noted in passing that its removal is an operating problem of considerable economic significance.

The benzylphenols were dissolved by adding the theoretical equivalent of sodium hydroxide; this was necessary due to the fact that the free benzylphenols are sparingly soluble while the corresponding phenates are quite soluble.



## Experimental Work

The work covered in this report included a study of bacterial relations under both summer and winter operating conditions. For these studies a system was available whose characteristics could be varied almost at will and which was so convenient that every change in operating conditions could be followed in detail. This system is installed in a general office in St. Louis and is briefly described as follows:

The air in the building is circulated through the equipment shown in Figure 1, where it is washed, humidified, and heated in winter, or dehumidified and cooled in summer. It passes through water sprays which control the humidity and cooling. Heating is effected by cast-iron steam coils placed after the washer. A turbine-type blower fan, located at the effluent side of the washer, forces circulation through the main and subsidiary distributing ducts to the separate floors and rooms, where the air is discharged from louvres at the ceiling. The return air is picked up by ducts at the ceiling and returned to a common duct which enters the washer just ahead of the washing sprays. Fresh make-up air from the outside passes through viscous-type filters and steam coils, and is mixed with the air returned from the building just ahead of the washing sprays. Very little fresh air is added, averaging less than 10 per cent during the warmer months.

The water used in the sprays for cooling and humidity control is chilled by passage through a shell-and-tube heat exchanger, using liquid ammonia as a refrigerant, and is circulated by a centrifugal pump. The water level in the tank of the washer is maintained automatically by a float valve connected with the city water supply and by an overflow pipe. The average temperature of the water in summer is about 44° F. There is a temperature rise of about 4–5° F. during passage through the sprays. No refrigeration is used during the winter months and the water temperature approaches that of the air. The system is carefully controlled and almost ideal atmospheric conditions are maintained in the building at all times.

Many methods have been proposed for the estimation of the bacterial content of air (3, 8, 16, 23, 25), but in the present work only the Petri plate method and the centrifugation method of Wells (18) were used. The bacterial content of the washing water was determined by collecting samples aseptically and plating various dilutions in nutrient agar (1). All plates were incubated for 48 hours at 37° C. The organisms which grow under these conditions are those which are most significant from the standpoint of health. The water in the washer was changed, and the equipment thoroughly scrubbed out before each test period.

### Winter Operation

At first the increase in bacterial count of only the water in the air-conditioning system was studied. When no germicide was added, the count increased rapidly, as shown by the upper curve in Figure 2. The increase was approximately a linear function and did not approach the logarithmic increase reported by Larson. On Monday of the following week the system was cleaned, and sufficient germicide (*o*- and *p*-benzylphenols) was added to the humidifier water to produce a concentration of 500 p. p. m. When the germicide had been added, the bacterial content was reduced to an average of 10 organisms per cc. and was maintained at this low figure for the duration of the test. The lower curve in Figure 2 shows the bacterial count of the water after germicide had been added. The ordinate scale for this curve is much larger than that of the upper curve. If the same scale is used for both, the lower curve becomes practically coincidental with the *x*-axis and cannot be distinguished. At the same time Petri plates containing nutrient agar were exposed to the air of the building to obtain samples of the bacterial flora. The bacteria obtained from both the humidifying water and from the air of the building were studied by cultural and by micro- and macroscopic examination. The organisms in both air and water were quite similar, and the following forms predominated:

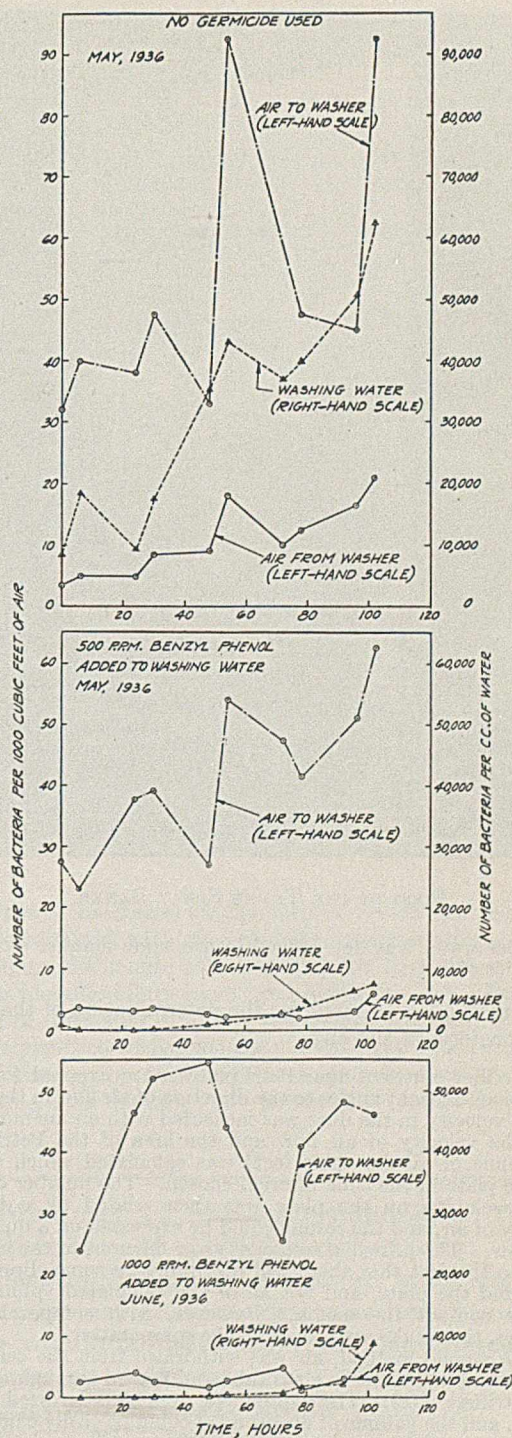
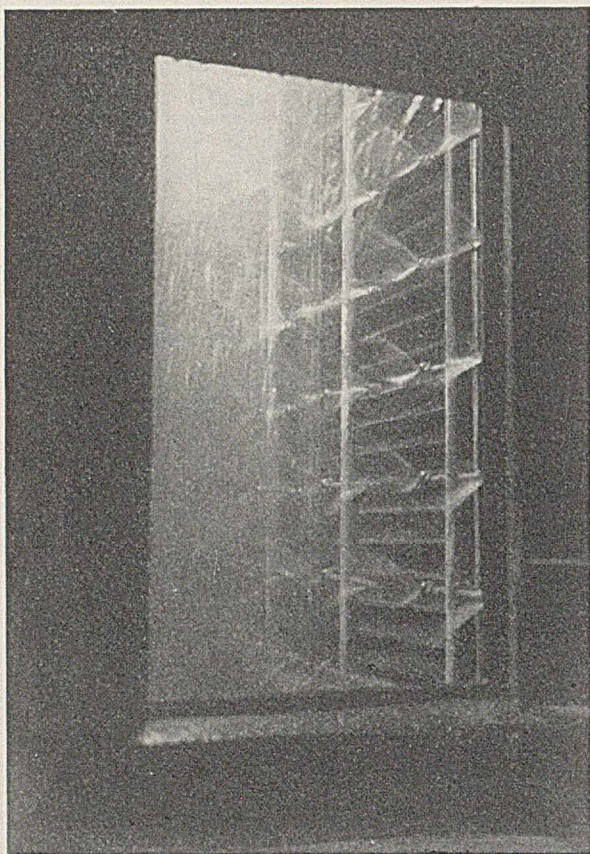


FIGURE 3. BACTERIAL COUNTS IN AIR-CONDITIONING SYSTEM

*Staphylococcus aureus, albus, and citreus*; diphtheroids; Gram-positive bacilli; pneumococci-like organisms; and fungi.

### Summer Operation

This series of tests differed from those just described in that accurate methods were used for the determination of the bacteria in the circulating air, and a comparison of the bacterial content of the air entering and leaving the washer was obtained. The bacterial content of air returned from the building (i. e., air before washing) was determined at a point in the middle of the return duct just prior to the point where it discharges into the washing chamber. The bacterial content of air delivered to the building (i. e., air after washing) was taken from the main duct about 15 feet beyond the fan. This position was chosen to minimize turbulence and the possible inclusion of droplets of humidifier water. The bacterial content of the



FIRST OF THE THREE SPRAY BANKS

humidifier water was determined in the same manner as in the first series of tests.

Two methods were used for the determination of the number of bacteria in the air:

In the first, nutrient agar Petri plates were exposed for definite periods at right angles to the direction of air flow in the duct. The air velocity in the duct was measured with an anemometer. From the velocity of air flow and the area of the Petri dish, the volume of air (in cubic feet) was calculated which should pass the plate in the time interval chosen. The number of bacteria developing on the plate was then related to a definite quantity of air, and the results could be expressed on a quantitative basis. The principal source of error inherent in the method is due to the fact that there will inevitably be some slippage of air around the plate, and not all of the calculated volume will actually contact the media. However, with comparable air velocities, the results are thought to be comparative.

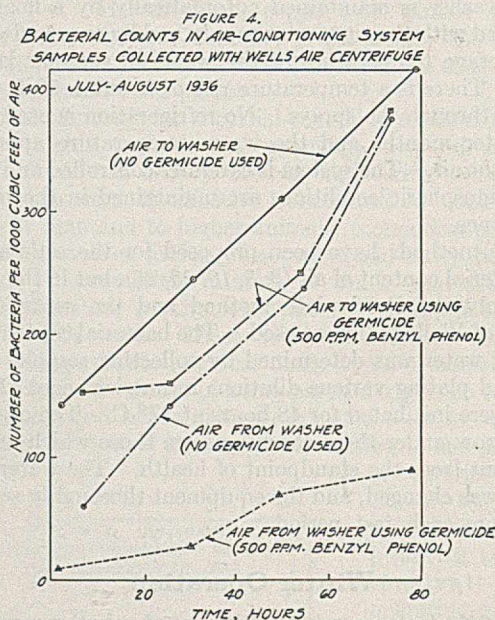
In the second method, air was withdrawn from the center of the duct through a sterile glass tube and passed through a Wells air centrifuge (18). The equipment was standardized as to air flow, and the volume of air sampled could be easily calculated from the rate of flow and time allowed for sampling.

Figure 3 shows the results obtained with the Petri plate method; Figure 4 gives those with the Wells centrifuge method. The results by these two methods are similar qualitatively but not quantitatively. The Wells centrifuge gives much higher values for both inlet and outlet air.

When the washing water is continuously recirculated and no germicide is added, the bacterial content increases steadily and more rapidly than in the case of winter operation. The bacterial content of the air returned from the building is substantially higher than that of the air delivered to the building. This behavior suggests that bacteria are removed from the air by washing, even though the wash water is rather highly contaminated with viable organisms. There is a steady increase in bacterial content of both sources from the beginning until the end of the week.

That the increase in bacterial content of the water is not due to growth of the bacteria initially present was proved by sealing a sample of the water in a sterile glass tube which was then suspended in the water of the air-washer pan. It was removed after 5 days, and the bacterial content determined in the usual manner. The initial bacterial count of 35,200 organisms per cc. increased only to 36,500. These results are to be expected when we consider that the temperature of the washing water is too low to permit rapid reproduction of the organisms which will grow at 37° C., the incubation temperature used in these tests.

The addition of benzylphenols results in the reduction of the bacterial content of the washing water to a very low figure. This reduction is accompanied by a striking reduction in the bacterial content of the washed air. There seems to be little tendency for the bacterial content of the washed air to increase over the weekly period, although the air delivered to the washer increases at about the same rate as when no germicide is used. In every case, however, the bacterial content of the air returned from the building to the washer is less when germicide is used than for a corresponding time when no germicide is used. The slight increase in the bacterial content of the washer water toward the end of the week results from a drop in the concentration of germicide present, caused by dilution by water condensed from the atmosphere during the process of dehumidification. Since the water capacity of the system is a constant, there is a continual loss of water through the overflow pipe during the times when dehumidi-



fication is taking place. Chemical tests showed that the actual concentration of benzylphenols present at the end of the week was as low as 15 p. p. m. Nevertheless, this small concentration greatly inhibited the increase in the bacterial content of the water and of the washed air. The most practical solution to this problem would be to add a small amount of germicide daily.

### Conclusions

The results seem to show that germicides of the benzylphenol type offer a cheap and convenient way to improve the efficiency of air-washing equipment in respect to bacterial removal. Only the physical measurements of bacterial reduction are reported, and no conclusion as to its possible hygienic significance can be made or inferred. In fact, the industrial application of germicides for the elimination of



mold and bacteria from air circulated for process work, such as in bakeries, breweries, and other fermentation industries, offers interesting possibilities entirely independent of the health aspect.

It is hoped that this work will stimulate interest among manufacturers of air-washing equipment toward the development of still more efficient apparatus for effecting bacterial control. Probably a higher degree of bacterial reduction than that reported here could be obtained by providing more intimate contact between the washing water and the circulating air, so as to prevent any short-circuiting of the air through the bactericidal sprays.

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RECEIVED September 21, 1936. Presented before the Division of Water, Sewage, and Sanitation Chemistry at the 92nd Meeting of the American Chemical Society, Pittsburgh, Pa., September 7 to 11, 1936.

# HEAT TRANSFER WITH Nonflammable Organic Compounds

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THE problems of heat transfer include applications in a multitude of industries. Convenience dictates their use in many simple installations in place of low-pressure steam. In some cases, temperatures above those of low-pressure steam are desired, without the complications of high-pressure systems. A related application is for still higher temperatures and greater heat transfer with a lower pressure than could be obtained with steam. In others, heat must be removed under conditions where an intermediate circulating medium is desirable instead of direct application of refrigeration.

### Media Used

The materials used for the purpose are so numerous and the purposes so varied that only a partial survey would be justified here.

By far the least expensive and most widely used heat transfer medium is water, in the liquid or gaseous phase. It has obvious disadvantages. At temperatures between 0° and 100° C. it is corrosive to many metals unless corrosion inhibitors are added (?). At temperatures above 100°, pressure is necessary; at temperatures below 0° salts must be added and the resulting medium is increasingly corrosive. Over 200°, pressures become high for saturated steam and efficiency poor for superheated steam. The use of fixed gases other than superheated steam is unimportant commercially.

The use of fused salts for the purpose is very old. Complex chloride mixtures with zinc chloride predominating (12, 13) and sodium dithionate solutions (31) are illustrative. Low-melting metallic alloys have been similarly used. Both are limited in their application by relatively high melting points and frequent corrosive attack. This field was broadened some years ago by the use of metallic mercury (10). It is applicable, over the range of -39° to 357° C., but the supply

Mixtures of tetrachlorobenzene, trichlorobenzene, dichlorobenzene,  $\alpha$ -chloronaphthalene, diphenyl, etc., show satisfactory characteristics as heat transfer media in laboratory and small-scale operative comparisons. Suitably selected mixtures are liquid from -50° to 200° C. The change of viscosity is moderate over this range as compared with competitive fluids. There is no appreciable corrosive effect on metals, even at high temperatures, in the presence of moisture. Evaporation at room temperature is slight. The mixtures are nonflammable over the range extending above their boiling points. They do not polymerize or sludge at high temperatures. Connections can be made with either metal hose or rubber substitutes. Toxicity presents no serious problem.

is strictly limited and the price high. Oxidizing conditions must be avoided, the vapors are highly toxic, and it amalgamates with nearly all metals except steel.

Oil as a heat transfer medium is mainly a substitute for water because of its higher boiling point. The supply is practically unlimited, the price not unreasonable. Disadvantages included sluggish flow at low temperatures, decomposition to give carbon residues (14) and sludges, and low thermal capacity. Oxidation must be avoided. Its use in cooling internal combustion engines has been recommended (25).

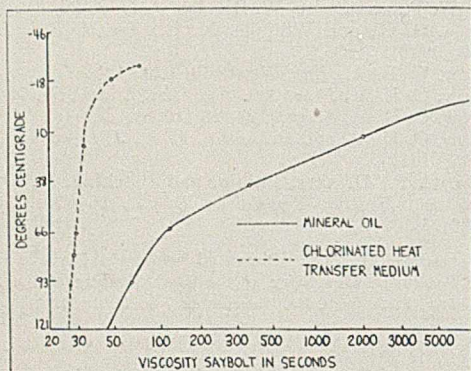


FIGURE 1. CHANGE IN VISCOSITY WITH TEMPERATURE

Diphenyl oxide with a melting point of 26° C. and a boiling point of 258°, or diphenyl melting at 69° and boiling at 255° are in use as a eutectic mixture melting at 12° (11, 15, 30). This melting point is sufficiently low to limit the possibilities of freezing in case of shutdown. Various mixtures have been used. Diphenyl oxide and carbon tetrachloride (6); diphenyl oxide and naphthalene, pyrene, or *p*-hydroxydiphenyl (5); diphenyl, diphenyl oxide, and naphthalene (20); and more complex mixtures (18). Addition of materials such as diphenylamine lowers the freezing point of the oxide, and mixtures have been produced with freezing points as low as -38° C. (21, 22, 23, 32).

The cost of such diphenyl or diphenyl oxide mixtures is not prohibitive, but their flammability and decomposition at elevated temperatures limit their use. The conditions for explosion of one of these mixtures containing diphenyl oxide and diphenyl have been studied (16). Related materials are secondary alkyl esters of polycarboxylic acids such as diisopropyl phthalate (19, 27), mixed dihydric alcohols (2, 3), diethylene glycol with or without additions (9, 28), mixed glycerol and ethylene glycol (24), vegetable oil containing oleic acid (8), and alkylated aromatic compounds (17, 26).

Halogenated compounds form another class. Those used included compounds of sulfur, oxygen, and fluorine such as SO<sub>2</sub>F<sub>2</sub> or SOF<sub>2</sub> (4), compounds of carbon chlorine and fluorine such as dichlorodifluoromethane, products of chlorination of diphenyl ketone (1), and complex condensation products such as those of chlorobenzene and chlorobenzyl chloride by the action of aluminum chloride (1).

Availability of chlorinated cyclic compounds suitable for the purpose still further expands the field. Trichlorobenzene is well suited for this purpose. It possesses the advantage of nonflammability. The commercial product is necessarily a mixture melting at about 11° and boiling at about 213° C.

In proper admixture with  $\alpha$ -chloronaphthalene, tetrachlorobenzene, dichlorobenzene, diphenyl, or several other materials, the freezing point can be lowered to -50° (29). The applicability over a wider range is offset by its inability to reach the higher temperatures without creating a pressure system. Laboratory data indicate the desirability of such a mixture

for commercial use, although it is not yet in large-scale use to the writer's knowledge. The data presented refer to a mixture of equal weights of commercial trichlorobenzene and  $\alpha$ -chloronaphthalene. Other data indicate similar results for several other mixtures.

### Viscosity Change

A typical set of viscosity data is that shown in Figure 1. The mixture used freezes at -37° C. The temperature-viscosity curve shows relatively small increase at temperatures down to below 0°. For comparison, a similar curve for a special grade of lubricating oil is superimposed as representing better-than-normal commercial results with oil. The curves are self-explanatory so far as comparison of the media is concerned.

### Corrosion

The corrosive effect of water is often serious; that of salt solutions when used for low temperatures is much more so. The effect of such a nonflammable compound was therefore determined by adding 1 per cent of water and refluxing with sheets of different metals individually for 10 hours. There was no weighable loss in the case of aluminum, cast and wrought iron, and galvanized iron. Losses of 2.3 mg. from 18 grams of copper and 2.1 mg. from 22 grams of brass were considered negligible. In no case did the specimens show visible evidence of corrosion. Although laboratory data on corrosive effects are frequently misleading, they can probably be accepted for the present as indicative of noncorrosive properties, in view of confirmatory plant experience with tri-chlorobenzene.

### Effect of Temperature

About 2 ounces of the mixture were heated in an open iron crucible at 160° C. for 46 hours. During that time about 90 per cent evaporation occurred. The remainder had not changed in physical properties, other than color by concentration of minor impurities, and no gummy residue or sludge had deposited on the sides or bottom of the crucible.

Since such a compound will necessarily be exposed to the air at times, in charging and otherwise handling it, the rate of evaporation was determined at room temperature of approximately 24°. The data are shown in Figure 2.

The compound evaporates when heated, without objectionable residue. This is confirmed by commercial practice of distillation of the chlorinated hydrocarbons from iron or

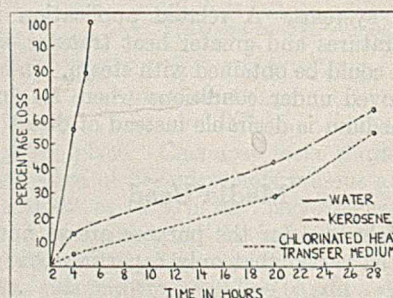


FIGURE 2. LOSS ON HEATING AT 41° C.

steel at atmospheric pressure without noticeable decomposition. Laboratory data are not available, however, on its decomposition in transition from the liquid to the vapor phase at pressures above atmospheric, in which sludging difficulties are encountered with many such media. From the structure and known stability of the material, it is improbable that decomposition will occur at those temperatures.

### Flexible Connections

Although flexible connections play no part in the use of the heat transfer media now in use, the adaptability of this mixture suggests its possible use for temporary set-ups of experimental equipment and for uses where a permanent heat transfer medium is not now utilized, such as in the gasoline engine of the automobile with suitable modification of radiator design, and in the Diesel engine.

Rubber hose is swelled by the mixture, as it is by so many organic solvents, and the solvent penetrates the hose. Flexible metal hose was used without deterioration. Hose lined with "Thiokol" showed no deterioration under some conditions but did deteriorate under others. Since the completion of this investigation, other resistant forms of rubber substitutes have appeared on the market, and probably more satisfactory connections are now available.

A thermal system was set up with a steel tube having two side arms. Each of these was connected to a glass tube for observation of circulation. The tubing used was of "Thiokol." The tube was heated externally, and, through change in specific gravity with temperature, the liquid was circulated for several weeks, 8 hours per day. No deterioration of the tubing or polymerization of the liquid could be detected.

### Toxicity

In commercial operation there are no recorded cases of serious toxic effects from the chlorinated cyclic hydrocarbons. Chlorination of an aromatic compound does not increase its toxicity but markedly decreases its volatility. The intensity of odor is in itself a protection, rendering exposure to toxic concentrations improbable.

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# The System Sulfur Dioxide- Decalin

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Thermal data have been obtained for the system Decalin-liquid sulfur dioxide. The critical solution temperature (C. S. T.) is 28.3° C. higher for Decalin than cyclohexane. The shape of the freezing point curve indicates a difference in solubility of the two forms of decahydronaphthalene.

ONE of the most useful refining agents in the petroleum industry is sulfur dioxide. Hence any data concerning solubility relation between this liquid and hydrocarbons should be of interest. The solubility relations between cyclohexane and sulfur dioxide were determined some time ago (1) but work on the relations between the dicyclic hydrocarbon decahydronaphthalene and sulfur dioxide has been held up because of the difficulty of preparing in the pure state either of the two isomers of this substance. It was, however, considered worth while to obtain the thermal data of the mixture of the *cis* and *trans* forms which is sold under the name of "Decalin."

The Decalin used was the ordinary commercial product sold by the British Drug House. It was distilled at 15 mm. pressure. The residue was slightly colored and its refractive index suggested the presence of Tetralin. The Decalin so obtained had a refractive index ( $n_D^{20}$ ) of 1.4736 and a density ( $d_4^{20}$ ) of 0.8795. It consisted, therefore, on the basis of the figures for the refractive index and density given in the International Critical Tables, of 72.5 per cent *trans* and 27.5 per cent *cis* form. The sulfur dioxide was prepared from c. p. sodium bisulfite and dried by passing over phosphorus pentoxide.

### Procedure

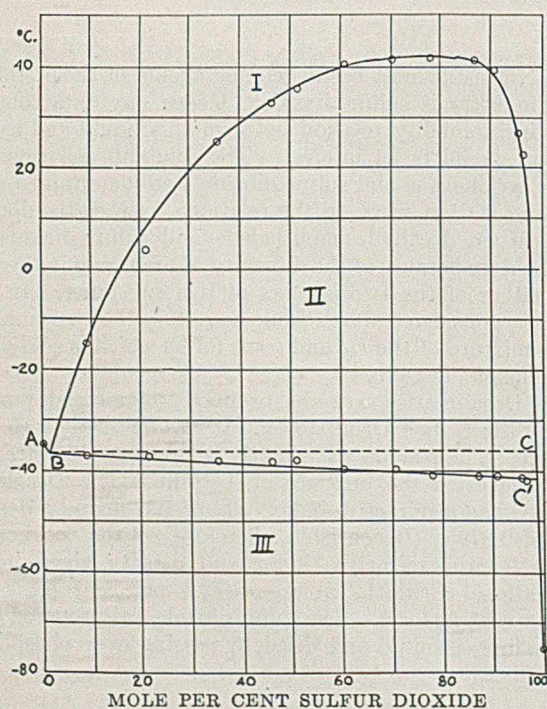
The bulb method was used for determining the freezing points and temperatures at which the two liquids disappeared. Known amounts of the hydrocarbon were put into the bulbs which were sealed to the sulfur dioxide filling apparatus, already described (2), and the desired amounts of sulfur dioxide introduced.

By cooling the liquid contents of the bulbs to -30° C., two liquid layers appeared. Each was then placed in a bath whose temperatures could be altered slowly. The bulbs were vigorously shaken while the temperature rose and the point at which the liquid became clear was taken as the solubility limit for that temperature at that particular concentration. The freezing point was measured by freezing the bulb contents until a considerable amount of crystals was visible.

The temperature was then allowed to rise until all but a few tiny crystals remained. It was then kept constant for some minutes until no change in the amount of the solid phase appeared to take place. Then the temperature was again allowed to rise slowly, and the point at which all the crystals disappeared was taken as the freezing point. All temperatures were measured by a standardized mercury thermometer above 0° C. and by a standard pentane thermometer below. The results are listed in the following table:

Weight of Decalin Grams	SO <sub>2</sub>		Temp. at Which One Liquid Disappeared ° C.	Incipient Freezing Points ° C.
	Grams	Mole %		
	0	0		
1.9455	0.0860	8.77	-14.90	-35.5
1.8942	0.2315	20.93	3.95	-37.3
2.0529	0.5146	35.06	25.20	-38.3
1.4815	0.6011	46.70	32.60	-38.4
1.3925	0.6611	51.67	35.50	-37.9
0.5419	0.3799	60.63	40.40	-39.6
0.4192	0.4564	70.23	41.35	-39.9
0.1668	0.2692	77.72	41.80	-40.4
0.3648	1.0910	86.58	41.65	-40.9
0.2226	1.0139	90.78	39.95	-41.1
0.2078	1.8629	95.15	26.80	-41.3
0.0588	0.6994	96.37	22.40	-41.9
....	....	100	...	-75.4

By plotting mole per cent sulfur dioxide against temperature, the curve in the figure is obtained. The critical solution temperature is thus shown to be 41.8° C. Region I contains one liquid phase; region II, two liquid phases; and region III, solid Decalin and one liquid. The peculiarity



about the diagram is the shape of line BC' along which the freezing points fall. It does not coincide with line BC because we are here dealing with a ternary system and the freezing points under the experimental conditions are not true equilibrium states. If the solubility of the two forms of the hydrocarbon were the same, there would not be this difference.

The C. S. T. for the dicyclic ringed compound with sulfur dioxide is thus 28.3° C. higher than that of cyclohexane and 4.5° higher than that of *n*-decane.

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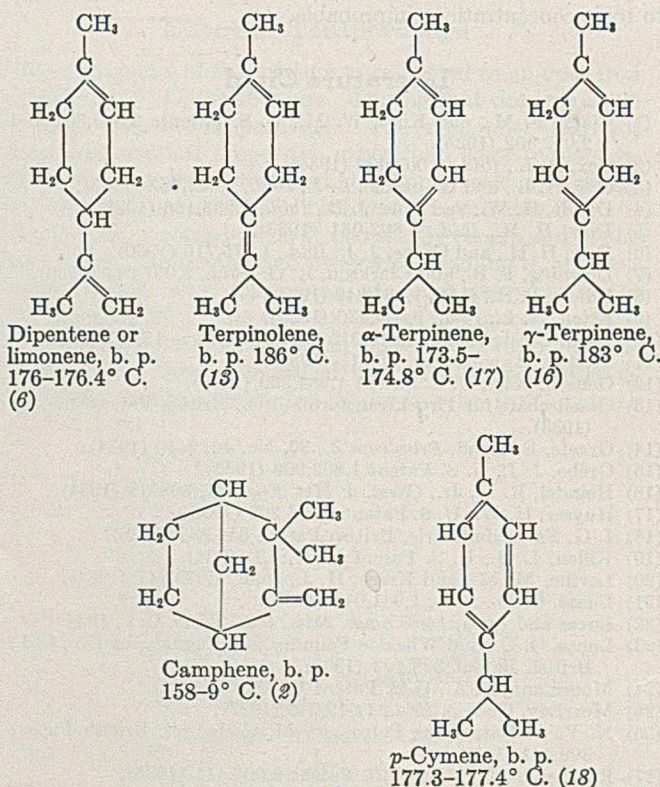
RECEIVED August 28, 1936.

# Isomerization and Hydration of Pinene

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THE study of the isomerization, hydration, and polymerization products of pinene as produced by the action of various agents (mostly acids) offers an interesting but complicated subject. Many products are formed, and, in spite of the large amount of published work, it appears to be almost impossible, except in a few cases, to control such reactions so as to obtain any one product in good yields.

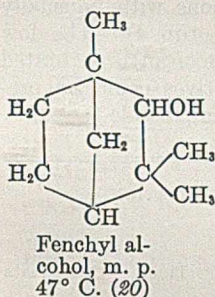
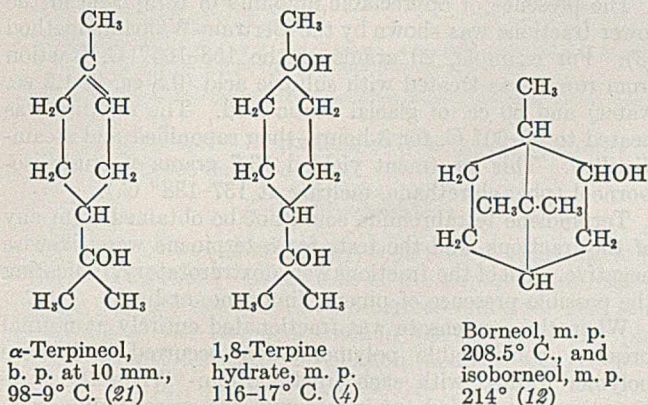
The isomerization of pinene has been reported by various workers to yield in varying amounts the following hydrocarbons:



Dupont (11) showed the value of Raman spectra in the analysis of such hydrocarbon mixtures. After treating pinene with 50 per cent sulfuric acid at a temperature not over 50° C. for 24 hours and working up the resulting mixture, he was able to show the presence of the following compounds: *p*-cymene, camphene, limonene,  $\alpha$ -terpinene,  $\gamma$ -terpinene, terpinolene, and 1,4-cineole. This probably

represents the most complete qualitative treatment to date. In general, however, the literature is vague both as to the constituents and the amounts present.

The same may be said of the isomerization and hydration of pinene but to a lesser extent. Although many papers and patents refer to the direct formation of  $\alpha$ -terpineol, terpine hydrate, borneol, and isoborneol or their derivatives, relatively few refer to actual yields. Small amounts of fenchyl alcohol have also been reported:



Because of the qualitative nature of so much of the earlier work and the conflicting statements in others, it was thought desirable to repeat some of the previous work under somewhat different conditions and at the same time investigate some new methods.

Sulfuric and phosphoric acids were used as isomerization agents.

In general, phosphoric acid was much less effective but similar in its action to sulfuric acid. Only the experiments with sulfuric acid are reported in this paper. In the acid isomerization, terpinolene was the only hydrocarbon which could be isolated in a relatively pure state by fractionation, and it was obtained in fair yields. Dipentene was always present in the 174-178° C. fraction but was never obtained pure. The presence of limonene could not be established in any of the runs by chemical means. It is extremely doubtful if the hydrocarbons present (165-180° C.) can be successfully fractionated. Conant and Carlson (9) experienced similar difficulties in the fractionation of mixtures of pinene and dipentene. *p*-Cymene was found in the 174-178° C. fraction in all cases examined, although in small amounts. At times tests for  $\alpha$ -terpinene (nitrosite, melting point 155° C.) were obtained in the range 174-183° C., but the results were not consistent and duplicate runs seldom gave the same data. Camphene, cineole, and  $\gamma$ -terpinene were not found.

An attempt was also made to isomerize pinene by passing its vapor over 20-mesh pumice impregnated with thorium

The isomerization and hydration of  $\alpha$ -pinene as produced by sulfuric acid and phosphoric acid were studied. Only terpinolene, terpineol, and terpine hydrate could be readily isolated in pure form. The vapor-phase isomerization of  $\alpha$ -pinene over heated thorium oxide was studied. The main product was dipentene with appreciable amounts of camphene.

oxide. This method yielded quite different results; the major product was dipentene with appreciable amounts of camphene.

Both sulfuric and phosphoric acids were employed for the hydration experiments. Again phosphoric acid, under the same conditions, proved much less effective. In these runs terpine hydrate and terpineol could be readily isolated. Hydration was never complete, and the reaction mixtures contained some mixed hydrocarbons, of which only terpinolene could be separated in a pure state. Small amounts of borneol were isolated in the runs where ethyl alcohol was not used.

Of the numerous experiments carried out, only the more important results are tabulated here. All of the results included were verified by duplicate runs. If the conditions are rigidly followed, fairly good check results can be obtained.

The pinene used was obtained from rectified American turpentine oil. It was allowed to stand over potassium hydroxide, steam-distilled, and dried. It was then fractionated over sodium. The 155-156.5° C. fraction had the following constants:  $d_{20}^{20}$ , 0.8665;  $n_D^{20}$ , 1.4777;  $[\alpha]_D^{21} + 16^\circ$ .

### Acid Isomerization, Liquid Phase

The pinene was added slowly, with vigorous stirring, to the cold sulfuric acid-ethyl alcohol solution, the rate being so adjusted that the temperature remained fairly constant. At the end of the reaction the two layers were separated; the upper layer was neutralized at once with sodium bicarbonate and then washed with water. The lower layer was added to water, when more oil separated. The latter was treated as just described and added to the first oil separated. The total oil was then steam-distilled to separate the polymer which was not volatile in steam. The steam-volatile oil, after drying over anhydrous sodium sulfate, was fractionated in vacuum (10 mm.) and finally fractionated at normal pressure over sodium. The final product was collected in the following fractions:

° C.	Fraction
156-161	Mostly pinene
161-170	Some pinene and dipentene (very small)
170-174	Impure dipentene (small)
174-178	Mostly dipentene and <i>p</i> -cymene
178-184	Dipentene and terpinolene
184-188	Terpinolene

The terpineol (vacuum fractions, 94-98° C. at 10 mm. pressure) was not fractionated at atmospheric pressure.

TABLE I. LIQUID-PHASE ISOMERIZATION

Run No.	Reagents Grams	Time of Addition		Total Time		Steam-Volatile Oil Grams	Polymer Grams	Terpinolene Grams	Terpineol Grams	Terpin Hydrate Grams	Recovered Pinene Grams
		Temp. ° C.	Hr.	Min.	Hr.						
1	136 C <sub>10</sub> H <sub>16</sub> , 46 C <sub>2</sub> H <sub>5</sub> OH, 49 H <sub>2</sub> SO <sub>4</sub>	0	3	15	4	0	109.6	10	34.3	4	0
2	272 C <sub>10</sub> H <sub>16</sub> , 92 C <sub>2</sub> H <sub>5</sub> OH, 98 H <sub>2</sub> SO <sub>4</sub>	- 8	8	15	8	75	237	26	66.7	17	4
3	136 C <sub>10</sub> H <sub>16</sub> , 46 C <sub>2</sub> H <sub>5</sub> OH, 49 H <sub>2</sub> SO <sub>4</sub>	-10	2	15	3	0	111.3	6.5	30	8	0
4	136 C <sub>10</sub> H <sub>16</sub> , 92 C <sub>2</sub> H <sub>5</sub> OH, 49 H <sub>2</sub> SO <sub>4</sub>	- 4	4	0	6	0	112.5	16	9.3	3	0
5	136 C <sub>10</sub> H <sub>16</sub> , 46 C <sub>2</sub> H <sub>5</sub> OH, 49 H <sub>2</sub> SO <sub>4</sub> <sup>a</sup>	0	1	30	3	0	48.7	74.5	24	0	0

<sup>a</sup> Allowed to come to room temperature and heated to 65-70° C. for 1 hour.

It was identified by means of its physical constants and the melting point of its nitrosochloride (107–108° C.).

The terpin hydrate settled out of the aqueous layer after the removal of the oil, on standing for 3 to 4 days. It was recrystallized from acetone containing a little water.

The terpinolene fraction, after several distillations had the following average values: boiling point, 184–187° C. at 760 mm.;  $d_4^{20}$ , 0.8583;  $n_D^{20}$ , 1.48017. These values were almost constant for the various runs. They check fairly well with the best values given in the literature. Semmler and Schosberger (19) gave: boiling point 67–68° C. at 10 mm.;  $d^{20}$ , 0.8520–0.8547;  $n_D^{20}$ , 1.48228–1.48484. Henry and Paget (13) gave: boiling point, 186° C.;  $d_{15}^{20}$ , 0.8633;  $n_D^{20}$ , 1.4883.

The terpinolene was further identified by means of its tetrabromide. The bromination was carried out in a cold ether–amyl alcohol solution, and yields of 50 to 60 per cent were obtained. In most cases the separation of the tetrabromide occurred readily. In some few cases the addition of a little ethyl alcohol facilitated the separation. After recrystallization from ethyl alcohol it usually melted at 115–116° C., the value given in the older literature. After repeated recrystallization from alcohol, the least soluble form was obtained which melted at 122° C. Henry and Paget were the first to show that the recrystallization of the tetrabromide yielded two forms. The first to come out melted at 122° and the second melted at 119° C.

At times, tests for  $\alpha$ -terpinene (nitrosite, melting point 155° C., 22) were obtained in the fractions at 174–183° C., but the results were not consistent and duplicate runs often gave negative results.

The presence of dipentene was established by means of its tetrabromide, melting point 124–125° C. It was the main constituent of the 174–178° fraction and was found in smaller amounts in the fractions 170–174° and 178–183° C. The limonene tetrabromide was not isolated at any time.

*p*-Cymene was usually found in small amounts in the 174–178° C. fraction. It was obtained from this fraction by repeatedly shaking with concentrated sulfuric acid and finally steam-distilling; the terpene hydrocarbons were polymerized and hence not volatile in steam (2,6-dinitro derivative, melting point 54° C., 7).

The lower fractions (except 156–161° C., mostly pinene) consisted definitely of mixtures. Various types of fractionating columns were tried but in no case was separation possible. The values for some of the intermediate fractions are as follows:

° C.	$d_4^{20}$	$n_D^{20}$
156–161	0.8509–0.8512	1.4658–1.4743
174–178	0.8480–0.8476	1.4734–1.4740
178–183	0.8472–0.8474	1.4743–1.4765

The fractions from 156–180° C. were dextrorotatory but varied from run to run, indicating the probable presence of pinene, limonene, or both. Repeated tests were made for camphene and cineole but always with negative results.

The polymer formed gave rather uniform values for physical constants, varying over a very small range: boiling point, 166–168° C. at 8 mm.;  $d_4^{20}$ , 0.9198;  $n_D^{20}$ , 1.50843. It appeared to be the same dimer reported by Dulou (10), Carter, Smith, and Read (8), and Brooks and Humphrey (7).

### Vapor-Phase Isomerization

Thorium oxide was the only catalyst studied in this series of experiments. Eighteen grams of 20-mesh pumice were impregnated with 6 grams of thorium oxide. The pumice was added to a nitric acid solution of the thorium, the solution slowly evaporated, and the residue gently heated until no more oxides of nitrogen were given off. A 4-inch (10.2-cm.) catalyst bed was held in place by perforated porcelain plates, in a 26-mm. (inside diameter) Pyrex tube. A regulated stream of nitrogen was bubbled through the heated pinene, and the mixture was then passed through a preheater and over the catalyst. Pyrolysis effects increased at higher temperatures, and it was found neces-

sary to operate within fairly definite temperature limits (380–425° C.). The condensate was worked up by repeated fractionation, either at normal pressure or in vacuum.

The presence of unchanged pinene was established by means of physical constants and the formation of the nitrolbenzylamine (melting point 122–123° C.). Dipentene was present in large amounts as indicated by the good yields (55–65 per cent) of dipentene tetrabromide from the 170–180° C. fractions.

The presence of appreciable amounts of camphene in the lower fractions was shown by the Bertram-Walbaum method (5). For example, 20 grams of the 158–165° C. fraction from run 1 was treated with sulfuric acid (0.8 cc. in 1.2 cc. water) and 50 cc. of glacial acetic acid. The mixture was heated to 50–60° C. for 3 hours, then saponified and steam-distilled. This treatment yielded 13.7 grams of crude isoborneol (phenylurethane, melting at 137–138° C.).

Terpinolene tetrabromide could not be obtained from any of the fractions, and the tests for  $\alpha$ -terpinene were likewise negative. All of the fractions were dextrorotatory, indicating the possible presence of pinene, limonene, or both.

When the condensate was fractionated entirely at normal pressure considerable polymerization occurred and more polymer formed with each fractionation. When the fractionation was carried out in vacuum, the excess polymerization was avoided and low-boiling fractions with unusually low densities were obtained (Table II, run 4). The low densities indicated the possible presence of an unsaturated open-chain hydrocarbon, but no derivatives could be prepared and fractionation appeared to be impossible.

TABLE II. VAPOR-PHASE ISOMERIZATION

Run No.	Pinene Used	Bath Temp.	Catalyst and Preheater Temp.	Nitrogen Rate	Time	Steam-Volatile Condensate
	Grams	° C.	° C.	Liters/min.	Hr. Min.	Grams
1	344	170	390	0.78	2 45	273
2	430	160	420	0.78	4 15	340
3	Same as 2, without catalyst	160	420	0.78	3 30	361
4	430	170	420	0.78	3 30	350
Analysis of Run 1						
	Fraction ° C.	$d_4^{20}$	$n_D^{20}$	$[\alpha]_D^{25}$		Steam Dist. %
	158–165 <sup>a</sup>	0.8445	1.4751	+10.1		22.1
	165–170	0.8445	1.4772	+14.4		18.8
	170–175	0.8421	1.4783	+18.6		21.8
	175–180	0.8420	1.4790	+21.8		33.0
Analysis of Run 2						
	158–165	0.8400	1.4760	+ 8.9		21.7
	165–170	0.8401	1.4788	+13.0		18.0
	170–175	0.8420	1.4811	+18.7		27.1
	175–180	0.8438	1.4822	+22.2		29.6
Analysis of Run 3						

The steam-volatile oil after several fractionations yielded 60 per cent of fairly pure pinene, whose constants checked the starting point quite well. The rest of the oil appeared to be a mixture of pinene and dipentene. Poor yields of dipentene tetrabromide were obtained on the higher boiling fractions.

Fraction at 10 Mm. <sup>b</sup>	Yield Grams	$d_4^{20}$	$n_D^{20}$	$[\alpha]_D^{25}$
51–2	16.1	0.8307	1.4783	+ 7.4
52–3	49.6	0.8275	1.4780	+ 8.9
53	27.7	0.8255	1.4777	+ 8.9
53–4	47.3	0.8258	1.4776	+10.2
54–54.5	17.5	0.8276	1.4787	+11.1
56–58	23.2	0.8356	1.4780	+10.8
58–58.5	26.3	0.8301	1.4788	+11.6
58.5–59	25.8	0.8273	1.4795	+12.1
59–60	43.6	0.8317	1.4819	+13.1
60–65	14.7	0.8555	1.4853	+12.4
65–71	14.9	0.8468	1.4922	+11.5

<sup>a</sup> Twenty grams of the 158–165° C. fraction yielded 13.7 grams of crude isoborneol by the Bertram-Walbaum method.

<sup>b</sup> The fractionation in vacuum proved less efficient than at normal pressure. All of the fractions from 54–71° C. gave tests for dipentene in spite of the low density. The lower fractions, 51–54° C., contained appreciable amounts of camphene but not as much as the 158–165° C. fraction from run 2; 98 grams gave 19.8 grams of crude isoborneol by the Bertram-Walbaum method.

TABLE III. HYDRATION

Run No.	Reagents Grams	Temp. ° C.	Time of Addition		Total Time		Steam-Volatile Oil Grams	Polymer Grams	Terpinolene Grams	Terpineol Grams	Terpine Hydrate Grams	Recovered Pinene Grams
			Hr.	Min.	Hr.	Min.						
1	136 C <sub>10</sub> H <sub>16</sub> , 46 C <sub>2</sub> H <sub>5</sub> OH, 49 H <sub>2</sub> SO <sub>4</sub> , 10 H <sub>2</sub> O	-5	4	0	5	30	124	2.9	28.7	24.8	2	17.5
2	136 C <sub>10</sub> H <sub>16</sub> , 46 C <sub>2</sub> H <sub>5</sub> OH, 49 H <sub>2</sub> SO <sub>4</sub> , 20 H <sub>2</sub> O	-3	2	15	5	0	112	2.4	10.2	38.4	2.2	20
3	136 C <sub>10</sub> H <sub>16</sub> , 46 C <sub>2</sub> H <sub>5</sub> OH, 49 H <sub>2</sub> SO <sub>4</sub> , 20 H <sub>2</sub> O	0	2	15	12	0	103	7	13.5	40.6	9.6	0
4	136 C <sub>10</sub> H <sub>16</sub> , 46 C <sub>2</sub> H <sub>5</sub> OH, 49 H <sub>2</sub> SO <sub>4</sub> , 20 H <sub>2</sub> O, 10 HgSO <sub>4</sub>	-3	2	20	5	0	121	3	5.1	44.3	1.6	25
5 <sup>a</sup>	136 C <sub>10</sub> H <sub>16</sub> , 49 H <sub>2</sub> SO <sub>4</sub> , 23 H <sub>2</sub> O	-3	4	0	7	30	48.4	20	8.1	10.8	57.8	0
6	68 C <sub>10</sub> H <sub>16</sub> , 49 H <sub>2</sub> SO <sub>4</sub> , 23 H <sub>2</sub> O	-8	2	45	5	0	24.4	3.1	3	3	30	15
7	68 C <sub>10</sub> H <sub>16</sub> , 49 H <sub>2</sub> SO <sub>4</sub> , 23 H <sub>2</sub> O	-3	3	30	8	0	26	6	0	2.5	34.5	13.6
8	136 C <sub>10</sub> H <sub>16</sub> , 98 H <sub>2</sub> SO <sub>4</sub> , 46 H <sub>2</sub> O	-3	4	30	6	30	46	9	4	7	98.5	0
9	136 C <sub>10</sub> H <sub>16</sub> , 98 H <sub>2</sub> SO <sub>4</sub> , 60 H <sub>2</sub> O	-2	3	20	6	20	45	8.8	2.9	5.1	100.5	5.2
10	68 C <sub>10</sub> H <sub>16</sub> , 49 H <sub>2</sub> SO <sub>4</sub> , 45 H <sub>2</sub> O <sup>b</sup>	0	1	30	10	0	66.8	3	..... Mostly unchanged pinene .....			

<sup>a</sup> In runs 5, 6, 7, 8, and 9, 1 to 3 grams of borneol were isolated in each case.

<sup>b</sup> Then stirred for 3.5 hours at 5° and 5 hours at 25° C.

Because of space limitations only a few of the more important runs are included here.

### Acid Hydration

The pinene was added slowly, with vigorous stirring, to the cold acid solution. In the case of the terpineol runs, the reaction mixture was treated as described under the acid isomerizations. The terpineol fraction was separated and purified by repeated vacuum distillation (boiling point 95–98° C. at 10 mm.;  $d_4^{20}$ , 0.9361;  $n_D^{20}$ , 1.4805).

The mixture was fractionated at normal pressure. Fairly pure terpinolene was isolated in every case and identified through its tetrabromide. Dipentene was also found in every case as indicated by its tetrabromide. Chemical tests failed to disclose the presence of any other hydrocarbons.

In the case of the terpin runs, the reaction mixture was poured into 100 to 200 cc. of ice water and allowed to stand overnight in the cold to facilitate the precipitation of the terpin hydrate. The latter was filtered with suction, washed with a little cold acetone, and recrystallized from hot acetone containing a little water (melting point 115–117° C.).

Small amounts of borneol or isoborneol separated during the vacuum distillation and sometimes during the steam distillation. It only appeared in those runs where alcohol was not used. It was identified by its melting point (200–203° C.) and phenylurethane (melting point 137–139° C.).

### Discussion of Results

The action of concentrated sulfuric acid on pinene is vigorous and difficult to control. Preliminary runs were made at temperatures ranging from 0° to -60° C. These runs were very unsatisfactory, and polymerization appeared to be the major reaction. In the presence of ethyl alcohol (ethylsulfuric acid being the probable isomerizing agent) the reaction proceeded much more smoothly although temperature control remained the most important factor. As Table I indicates, some hydration usually occurred in these runs. In the presence of larger amounts of alcohol (run 4) the reaction became much slower and considerable amounts of unchanged pinene were recovered. In run 5, where the temperature was finally raised to 65–70° C., a fair amount of terpinolene was obtained. Terpinolene has been reported to be unstable and easily isomerized and polymerized.

The catalytic vapor-phase isomerization was of interest, chiefly because of the possibilities indicated. A more complete examination of various catalysts would undoubtedly lead to better yields of camphene.

Mulsey (14) passed pinene vapors over aluminum oxide at 310–425° C. At 410° he reported a large proportion of dipentene, a little limonene, no camphene, and probably some  $\alpha$ -terpinene and terpinolene.

Arbuzov (1) studied the isomerization of  $\alpha$ -pinene over hot reduced copper and through tubes filled with fragments of Suprax glass. In addition to dipentene, he obtained an aliphatic hydrocarbon (C<sub>10</sub>H<sub>16</sub>, b. p. at 16 mm., 87–87.5° C.).

The best yield (26 per cent) of the latter was at 340–350° C. This compound was *allo*-ocimene. Arbuzov concluded that temperature rather than the nature of the catalyst played the important role and probably this hydrocarbon was always formed when pinene was heated above 300° C.

Although it is possible that the results obtained might be explained by the presence of *allo*-ocimene, there was no positive evidence on which to base such a conclusion. It was not possible to isolate such a hydrocarbon, and it was extremely doubtful that the physical constants for the various fractions gave much indication of its presence. When the pinene was passed through the Pyrex tube without the catalyst, other conditions being the same, there was no indication of the presence of an unsaturated open-chain compound.

The hydration experiments (Table III) were, as a rule, easier to control because it was simpler to maintain a uniform low temperature. But here also temperature control appeared to be the most important factor; if the temperature was allowed to rise appreciably, considerable polymerization occurred. The best yields of terpineol resulted when ethyl alcohol was used; the absence of ethyl alcohol, other conditions being the same, facilitated the formation of terpin hydrate. It was surprising that no terpin hydrate separated when 50 per cent sulfuric acid was used (Table III, run 10) even though stirring was maintained for 10 hours.

Aschan (3) reported a 53.2 per cent yield of terpin hydrate by the use of 45 per cent sulfuric acid and stirring at 1° C. for 10 hours. Ono (15) reported a yield of 83 grams of terpin hydrate from 100 grams of pinene. He used 45 per cent sulfuric acid and stirred for 15 hours at 0° C.

The present experiments indicated a slow reaction where 50 per cent sulfuric acid was used.

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RECEIVED May 29, 1936.

# Pulps from the Whole Cotton Plant

## Comparison of Soda and Nitric Acid Pulps

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**T**HE utilization of the whole cotton plant as a possible source of material for the production of alpha-cellulose has occupied the attention of workers in this laboratory for several years. Dockery (8) showed that the mature plant contains approximately 80 per cent cellulose, but objections were urged that this cellulose was different, at least structurally, from that obtained from wood, and could not be used in the industry. Sanders (11) made alpha-cellulose and derivatives from three commercial woods and compared them with the corresponding products from the whole cotton plant. Identical x-ray diffraction patterns were obtained for any particular product, irrespective of the source of the cellulose; but x-ray results are determined by the orientation of the atom groups, and the data at present available do not suffice to distinguish between several possible structures. Dark-field microscopic studies with the Spierer lens failed to show any significant difference in the micelles of the cellulose from the several sources (2).

Since neither atomic nor micellar studies gave evidence of differences in cellulose that would affect its use, it seemed desirable to make cellulose pulps from the whole cotton plant by methods comparable with industrial practice rather than the purely laboratory procedures cited.

### Previous Investigations

Aside from articles relating to the present project, there are no references in the literature to the pulping of the whole cotton plant. Investigators have obtained promising results with various parts of the plant. The use of cotton linters is well known. Golova (3), after expressing the oil, treats the cottonseed meal with caustic soda and obtains a product (hull fiber) which is used like cotton linters to make rayon. Lur'e (6) makes wrapping paper from cotton stems by a treatment with caustic soda. Yakimanskiĭ (13) claims that the addition of 25 per cent of a cotton stem pulp to the ordinary wood pulp increases the mechanical strength of the resulting pulp. Shikata and Akagi (12) treat cotton stems with nitric acid, followed by a treatment with caustic soda and bleaching, to give a pulp of 87 per cent alpha-cellulose, suitable for rayon manufacture. Korzhenevskii and Raskina (5) use a similar process on cottonseed hulls, cotton stems, and reeds to give a pulp superior to that obtained by the usual methods of preparing pulps.

### Processes Used

Several different processes for making alpha-cellulose are utilized commercially. In order to test the material and results by as widely varying methods as possible, two radically contrasting processes were used: (a) the alkali or soda process and (b) the nitric acid process. An advantage of both of these processes is that pressure cooks are not essential. The soda process is frequently carried out under pressure when using wood chips, but the physical nature of the material of the present investigation indicated that pressure would be unnecessary.

Citations from the extensive literature on the soda process are not necessary here; but the nitric acid process is of recent development and is apparently used on a commercial scale in only a few plants. Pressure cooks are not used in this process. Essentially, it consists of treating the material with a weak solution of nitric acid (0.2 to 5.0 per cent) at temperatures varying from 80° to 100° C. for 15 to 120 minutes, washing, and then treating with a solution of caustic soda (0.5 to 3.0 per cent) and sodium sulfite (0.1 per cent) and 100° C. for 30 minutes to 4 hours. Lynch and Goss (7), Payne (9), and Hachihama, Onishi, and Takemura (4) used this process with bagasse and report excellent results. Shikata and Akagi (12) and Korzhenevskii and Raskina (5) used it with cotton stems. It is claimed that the successive acid and alkali treatments dissolve the lignins, pentosans, and other incrusting materials more efficiently than do the usual pulping methods. The presence of these materials in colloidal dispersion in the nitric acid solution, it is claimed, prevents a degrading action by the acid on the cellulose. The nitric acid process appears to be especially useful for lignocellulose material and is possibly preferable to the older processes.

### Raw Material

The material used in the present investigation consisted of the whole cotton plant, including the lint which had been grown and harvested during the 1930 season at Rockingham, N. C. (8). It was baled in the field and had been stored indoors at Chapel Hill since baling. It was run through a hammer mill of the type used on farms to prepare stock feed. The resulting ground material was a fluffy, uniform mixture. A small proportion of woody stems, approximately



an inch long and 0.25 inch in diameter (25 × 6 mm.) was well dispersed through the mass. This fluffy material was extracted with carbon tetrachloride in a Soxhlet apparatus holding about 3000 grams of the ground plant. The extract was decolorized with norite during extraction. The yield of oil was about 5 per cent of the weight of the whole plant. It was a soft solid at 20° C. By centrifuging and chilling, it was separated into an oil similar to cottonseed (85 per cent) and a wax (15 per cent). Extraction and refining of the oil will be described in another paper. The extracted plant lost all adhering carbon tetrachloride by a short exposure in air, absorbed the pulping solution easily, and was in an excellent condition for pulping.

### Processing

For pulping by the soda process, an apparatus was constructed like a double boiler. A large galvanized-iron can with a top was used as a steam bath. Within was a smaller can with a tight cover. The ground extracted plant was placed in the inner can, and dry steam was introduced at the bottom of this container. A current of steam was run into the outer galvanized-iron can near the top and discharged at the bottom.

The grams of material in the alkali treatment were as follows: whole plant, 1568; water, 7840; sodium hydroxide, 784; and sodium carbonate, 196. These proportions were suggested by an expert industrial pulp chemist, although the proportion of chemicals is greater than a survey of the literature would suggest. The mixture was boiled for 8 hours, and then the material was washed with warm water until it remained clear. Agitation was not used and the process required more than 24 hours. At this stage, the material was soft but not fully disintegrated. Matted bunches of cotton fibers, pieces of woody stems, and particles of seed meats were recognizable. The wet pulp weighed 2769 grams. It contained about 80 per cent water so that the dry pulp would weigh 554 grams, a yield of 35 per cent of the dry weight of the whole plant.

For the nitric acid process, a similar set-up was used except that the inner can was replaced by a large round-bottom flask. The following mixture was used:

Whole plant, grams	1000
Water, grams	7840
Nitric acid (sp. gr., 1.43), cc.	180

This is a 2.1 per cent solution of nitric acid. The plant material was wet thoroughly with hot water, and the whole was heated to about 70° C.; the nitric acid was added and then the rest of the water, hot. The temperature was raised as quickly as possible to 85–90° C. and maintained for an hour. The mixture was then washed with cold water in the flask until neutral to methyl orange. It was heated at 85–90° C. for 3 hours with 1 per cent sodium hydroxide solution and 0.1 per cent sodium sulfite solution, and washed at first in the flask and then by decantation and suction until the wash waters were neutral to phenolphthalein and were a light straw color. The pulp at this stage was similar to the soda pulp after the boiling treatment—i. e., soft but not fully disintegrated. The wet pulp weighed 2750 grams and contained 85 per cent water. Hence, the yield of dry pulp was 412.5 grams or 41 per cent.

Several methods of beating and bleaching were tried. Beating was imitated fairly successfully by grinding in a ball mill until the woody portions were disintegrated and the resulting pulp was a uniform paste. Both pulps were bleached by the Rue and Sconce method (10), using varying amounts of chlorine in the acid bleach and 1 per cent in the alkaline bleach. After bleaching, the first wash water was made just acid. In the case of the soda pulp, the best result was obtained with 10 per cent of chlorine in the acid bleach;

in the case of the nitric acid pulp, 12 per cent was desirable. With both pulps the best results were obtained with a consistency of 1 per cent. Accurate yields could not be obtained because of unavoidable mechanical losses in the ball mill.

### Analysis of Pulps

The pulps were analyzed for alpha-, beta-, and gamma-cellulose by the volumetric method of Bray and Andrews (1). Ash determinations were made on separate samples. In the case of the nitric acid pulp, analysis of five samples gave from 86.7 to 94.0 per cent alpha-cellulose. Two typical cases are given. Results are calculated on the basis of the oven-dry weight of the bleached pulp:

	Soda Pulp	Nitric Acid Pulp	
Alpha-cellulose	81.4	89.8	87.0
Beta-cellulose	0.3	1.2	2.5
Gamma-cellulose	8.2	2.6	4.1
Ash	8.8	6.3	6.3
Total	98.7	99.9	99.9

The high ash content of the pulps is due to the methods of harvesting and unprotected storage. If the ash is neglected, the alpha-cellulose for the soda pulp is 90.5 per cent and for the nitric acid pulp, 95.5 and 94.0 per cent.

### Conclusions

These results indicate that it is feasible to make a pulp with an alpha-cellulose content suitable for rayon and other industrial uses from the whole cotton plant. It is possible to recover a merchantable oil in good yields from the ground plant; the resulting extracted plant, because of the absence of water-repellent oils and waxes, is in an excellent condition to absorb the pulping solution. For this reason, boiling under pressure is not essential as with wood chips. In any commercial development it will be important to harvest and store the material under conditions which will keep contaminating sand and dust at a minimum. There is no problem of deterioration on storage. The results obtained with the nitric acid process harmonize with those obtained by Payne (9) and by Hachihama, Onishi, and Takemura (4) on bagasse, and suggest that a better yield and a purer alpha-cellulose are obtained by this process than by the usual pulping methods. These results suggest further that the nitric acid process is especially effective for lignocellulose material.

### Acknowledgment

Acknowledgment is made to Nicholas W. Dockery of Rockingham, N. C., for supplying the plant material used in this work.

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RECEIVED July 28, 1936. Presented before the Division of Cellulose Chemistry at the 92nd Meeting of the American Chemical Society, Pittsburgh, Pa., September 7 to 11, 1936.

# SUGGESTED PROCEDURE IN DESIGN OF Sheet Asphalt

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The procedure described consists of determining the brittleness of briquets by tumbling them in a revolving drum. When the percentage loss after an hour is plotted against the percentage asphalt, a characteristic curve is obtained which shows that the safe range of asphalt is that which corresponds to a brittleness range between 0 and 2. Briquets within this range of brittleness are then subjected to a stability test which consists of determining the load necessary to force a sphere,  $\frac{3}{4}$  inch (1.9 cm.) in diameter, into the specimen to a depth of  $\frac{3}{8}$  inch (9.5 mm.). This test shows that the stability decreases when the proportion of filler increases beyond a certain value, depending upon the quality of the sand. The combination of these two tests determines specifically the best proportion of asphalt and filler to be used with a given sand.

**T**WO of the most important variables to be determined in the design of sheet asphalt are the proper proportion of asphalt and fine aggregate (filler) to sand. The requirements of a good mixture are well known though not specifically defined. It frequently suffices to establish the best of several possible combinations. The methods of testing, therefore, are relative rather than absolute.

Until recently the "pat" test was generally used to determine the proper proportion of asphalt (20). It is still used extensively as a field test, and experienced technologists believe it to be reliable. The character of a stain made by a test specimen on paper indicates whether the mixture is too rich or too poor in asphalt. The simplicity of this method argues in its favor. Its disadvantages, on the other hand, are obvious. It is highly empirical. Years of experience are necessary before the appearance of the stain can be correctly and reliably interpreted in terms of percentage of asphalt.

A number of investigators held that the percentage of voids in the aggregate is an indication of the amount of asphalt to be used. This, to a large extent, is true. On the other hand, it is well known from service records that the best paving mixture is not that containing the minimum percentage of voids (4, 12). This can be explained by the fact that, since asphalt does not "wet" the aggregate perfectly, some air films and air pockets are unavoidable (3). The absolute volume occupied by air cannot be reduced, and only the apparent percentage of voids is reduced by increasing the

percentage of asphalt. The resulting mixture is consequently too rich. It is also known that films of asphalt are thinner than films of air and liquids generally used to determine the percentage of voids (12). Thus the percentage of voids determined by such methods yields values which are too high in reference to asphalt.

The desirability of some voids in the compressed mixture may be of a more fundamental nature. Pavements which gave perfect service for several years, were known to fail under service suddenly for no readily recognized cause. This is accounted for only by the assumption that continuous compression under traffic reduced the percentage of voids below the safe minimum (12). The likelihood of this assumption is supported by the fact that the strength of an asphalt pavement is due largely to the friction and interlacing of the irregular particles of the aggregate (8). Under traffic, owing to internal wear, the particles are crushed, the irregularities are reduced, and the interlocking effect is destroyed. It is interesting to speculate as to whether a superior paving could not be designed with round particles, provided a sufficiently stable asphalt could be found. At any rate, the initial percentage of voids in the aggregate cannot serve as a measure of the amount of asphalt to be added. The ultimate percentage of voids desirable in the finished pavement will depend on the asphalt, the kind of aggregate, and the shape of its particles.

Since 1924 several methods have been proposed for measuring the resistance to deformation of compressed test specimens. These stability-determining tests have become the most important tools in the design of paving mixtures. Of the numerous methods suggested, those of Hubbard-Field (11) and Skidmore are the best known and most widely used. The underlying principles of both methods are identical. The former is suitable for a specimen made of fine aggregate; the latter is adaptable to mixtures made with coarse aggregate. Both determine the total force required to shear completely parallel faces of the test piece.

The chief limitations of these devices are described by Hubbard (10): "We do not know yet what values to assign to the stability test; i. e., it may be best to work for a range that will be considerably below the maximum. However, we now have a yardstick for measuring stability, and the most satisfactory range is obtained by correlation of test results with the service behavior of pavements which have been subjected to the test."

The Hubbard-Field stability test employs a static force until a cylindrical specimen, 2 inches (5 cm.) in diameter and 1 inch (2.5 cm.) in depth, is completely forced through a ring  $1\frac{3}{4}$  inches (4.4 cm.) in diameter. On the other hand, the forces under actual traffic conditions are impact forces which are more severe than static forces of the same magnitude. To simulate actual service conditions more closely, Tarwater developed a rolling-stability testing machine (19). This consists of a revolving bank carrying eleven rollers. During the test, while the bank revolves, its entire weight (450 pounds or 204 kg.) rests upon the test specimen, which is held in a collapsible mold open on one end near the surface to allow displacement of the material. The number of revolutions required to produce a displacement of 0.3 inch (7.6 mm.) is considered to be an index of stability.

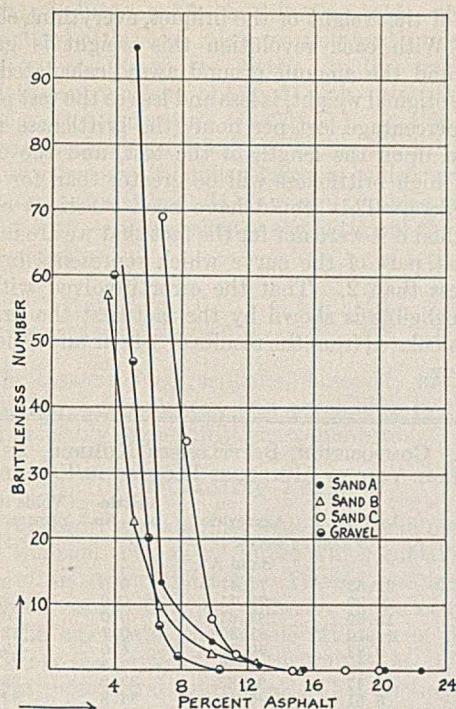


FIGURE 1. BRITTLINESS NUMBER vs. PER CENT ASPHALT BY WEIGHT

A reliable interpretation of the results of all these stability tests is impossible unless a service record of similar mixtures is available. This is a severe handicap not only to the research man, who works with new materials which have never been tried in service, but also to the highway engineer, inasmuch as the performance of a paving mixture in service depends upon so many variables that it is frequently well nigh impossible to correlate failure to any one factor.

It is desirable, therefore, to develop tests, the results of which could be readily interpreted without the need of a vast experience or a priori knowledge of the service records. These should enable the research man to determine the best composition and study the variables essential to obtain such mixture; and the highway engineer should be able to decide whether a newly proposed material shows sufficient promise to justify large-scale trials, which in the end must be the final test.

The tests are to establish the highest resistance to fracture and deterioration under impact and the greatest resistance to deformation under load at the highest temperature encountered in service—i. e., 60° C. (6). It is assumed that a mixture which answers these qualifications is of sufficient promise to justify large-scale trials.

The procedure described, developed, and used in this laboratory since 1933, seems to satisfy these requirements. In their present form the testing devices are not free from objections, but the procedure has possibilities and it is thought worth while to bring it to the attention of others.

### Brittleness Number

It is generally recognized that all stability tests should be accompanied by some brittleness or fracture test, for it is possible to design a mixture which will possess a high resistance to deformation and yet fracture and deteriorate under a frequent repetition of small impact forces. On the other hand, an intuitive analysis suggests that the brittleness of a specimen is likely to be a function of the proportion of asphalt present. As the proportion is increased to a large excess, the brittleness of the mixture will approach that of asphalt

alone, whereas, when the asphalt proportion is below the required minimum, the brittleness will increase sharply. Upon the assumption of this principle the following brittleness apparatus was built.

### Apparatus and Experimental Procedure

The brittleness was determined in a machine which consists of a cylindrical drum, 24 inches (60.96 cm.) in diameter and 24 inches in length, mounted horizontally on shafts welded into the ends of the drum. The shaft does not go through the drum. On the inside of the drum is welded a shaft, 4 inches (10.2 cm.) wide, from end to end parallel to the axis of rotation and bent at an angle to the shell so that at each revolution the specimen is picked up once, carried to the maximum height, and allowed to fall freely. It rotates 27 r. p. m. The shell is perforated with six rows of  $\frac{3}{8}$ -inch (9.5-mm.) holes so that all fines are allowed to sieve through, thus avoiding any cushioning effect and abrasion. The specimen is introduced through a small door at one end.

The test briquets were made in collapsible molds in the following manner. The aggregate, kept in a steam-jacketed pot at 150–160° C. for not less than 24 hours, was weighed and added to a previously weighed and melted amount of asphalt in a steam-heated pot. Mixing was done by hand until it appeared to be homogeneous to visual inspection. The collapsible mold, previously preheated and provided with a hopper, was filled with a generous excess of the hot mixture, tamped by hand, and then compressed under 2500 pounds (1134 kg.). The pressure was allowed to remain for 5 minutes.

The pressure was then released, the hopper removed, and the excess mixture struck off to the proper level by means of a hot knife. The briquets remained in the molds not less than an hour and were allowed to age at least 24 hours. Six briquets were made from each batch. All tests were made on specimens from the same batch. Each briquet weighed from 700 to 750 grams and was  $6 \times 2\frac{1}{2} \times 1\frac{1}{2}$  inches ( $15.24 \times 6.35 \times 3.81$  cm.) in size.

The briquet was weighed, allowed to remain in the refrigerator for at least 24 hours, and then rotated in the tumbler for an hour at room temperature and weighed again. The percentage loss in weight after an hour is defined as the brittleness number.

### Materials

Although several different asphalts and fillers were used in this study, mixtures with only one asphalt and one filler are considered sufficient to demonstrate the procedure of testing employed.

The materials are described in Table I. Sand A is the type used by local railroad companies for engine traction. Sand B is a quality available in this locality and generally used in making Portland cement concrete. Sand C was prepared in the laboratory by crushing stone and grading it by hand. The grading adopted is similar to that used by the U. S. Bureau of Public Roads (15). The particles of sands A and B are round, those of sand C are flat and angular.

TABLE I. CHARACTERISTICS OF MATERIALS USED IN THIS INVESTIGATION

Grading— Passing sieve No.	Retained on sieve No.	Per cent by weight		
		Sand A	Sand B	Sand C
8	10	16.9	...	...
10	20	2.5	26.7	3.9
20	30	55.5	25.2	6.4
30	40	38.5	25.2	10.3
40	50	3.0	3.7	14.2
50	80	0.5	1.0	30.9
80	100	...	0.6	16.8
100	200	...	0.4	16.7
200	...	...	0.3	0.8
Shape of particle		Round	Round	Flat and angular
Specific gravity		2.605	2.586	2.608
Per cent of voids <sup>a</sup>		37.7	32.6	42.89
Limestone:				
Specific gravity			2.585	
Per cent retained on No. 200 sieve			20.0	
Per cent of voids <sup>a</sup>			36.5	
Asphalt penetration in 5 sec. at 77° F. (25° C.) under load of 100 grams				35

<sup>a</sup> Determined by the Cone method (6, p. 206).

### Discussion of Results

The experimental data representing averages of three tests are given in column 4, Table II. Columns 2 and 3 show the percentages by weight of asphalt and aggregate, respectively. Column 5 gives the corresponding percentage of voids in the compressed mixtures. The percentage of voids was calculated by the following formula:

$$V = 100 - D \left( \frac{M}{S} + \frac{A}{Q} \right)$$

where  $V$  = per cent voids in compressed mixture  
 $D$  = apparent density of compressed specimen  
 $M$  = per cent of weight of aggregate  
 $A$  = per cent of weight of asphalt  
 $S$  = true density of aggregate  
 $Q$  = density of asphalt (1.0)

The density of the sample was determined by weighing the dry specimen, immersing it in 50 per cent alcohol for an hour, and measuring its volume by displacement in 50 per cent alcohol.

In Figure 1 the brittleness numbers are plotted against the percentage weight of asphalt. Each curve has a well defined "knee," which extends over a range of 2 or 3 per cent asphalt. The branch to the left is very abrupt.

Bearing in mind the almost unavoidable difference in proportioning, which exists between laboratory specifications and field plants, these curves, without any need of other tests, determine the safe minimum proportion of asphalt to be used—viz., that which corresponds to a brittleness number no greater than 2. For no matter how desirable other properties of mixtures corresponding to the upper part of the knee may be, no highway engineer will consider it safe to design a mixture so dangerously near the sharp rise of the curve. It so happens, as will be shown in the next section, that the maximum stability also corresponds to the lower portion of the knee in the brittleness curve.

These curves also explain the generally known fact that the range of asphalt variation is dangerously narrow, when the percentage of filler is high. Figure 6 gives curves representing the effect of increasing proportions of filler upon the brittleness number. The curves for 10 and 15 per cent filler almost coincide. In the case of 20 per cent limestone dust the range of asphalt variation is narrower. Mixtures containing 20 per cent filler, on the other hand, show a more abrupt change in the brittleness curve and at higher asphalt content. The actual rise of the brittleness curve is much sharper and the knee is shorter than those shown in these curves when effects of temperature and loss in weight are considered. This behavior will be discussed in subsequent paragraphs.

This test, therefore, seems to be a valuable yardstick for the determination of a safe minimum percentage of asphalt to be used with a given combination of aggregates. On the other hand, it is not sufficiently sensitive to differentiate between different kinds of aggregates and proportion of filler. In a complete procedure of design it should be supplemented by stability test. Any stability test will serve the purpose. However, the test described in the next section seems to have pronounced advantages.

The limitations of the brittleness test are as follows: Although this test is only remotely similar to the Deval abrasion test for bricks (1), the characteristics of both are to some extent analogous. It is known that abrasion is not proportional to the weight, and it was shown that the volume and shape factors are important and that the edge effect is considerable (13). This is true in the case of the brittleness test. The weight of the briquet, on the other hand, plays a much more important role in the brittleness test than it does in the Deval abrasion test. The amount ground away per revolution is proportional to the force of impact, and this is

a function of the weight of the briquet, everything else being constant. With each revolution this weight is gradually decreased, and the amount ground away, calculated on the basis of the original weight, is less and less as the test proceeds. Thus the percentage lost per hour (the brittleness number) will depend upon the length of the test, and the error for briquets of high brittleness will be greater than for those of low brittleness. This would have been a serious objection to this method if it were not for the fact that we are interested only in that part of the curve which represents brittleness numbers less than 2. That the error involved within this range is negligible is shown by the fact that the brittleness numbers calculated from the results of 1-hour and 3-hour tests check closely.

TABLE II. COMPOSITION, BRITTLNESS NUMBER, AND PERCENTAGE VOID OF MIXTURES PLOTTED IN FIGURE 1

No. of Mixture	Asphalt Per cent by weight	Aggregate	Brittleness No.	Voids in Compressed Sample %
		Sand A		
1	22.53	77.47	0.0	2.3
2	20.29	79.71	0.0	3.7
3	15.39	84.61	0.0	6.5
4	12.70	87.30	0.7	12.5
5	9.83	90.17	4.5	19.5
6	6.78	93.22	13.5	26.4
7	5.17	94.83	33.2	29.7
8	3.51	96.49	84.8	32.4
9	2.66	97.34	93.0	33.6
		Sand B		
36	15.39	84.61	0.0	1.3
37	12.70	87.30	1.0	7.6
38	9.84	90.16	2.5	12.5
39	6.78	93.22	9.8	20.3
40	5.17	94.83	22.6	22.6
41	3.50	96.50	57.0	26.2
		Sand C		
63	20.00	80.00	0.0	3.8
64	17.90	82.10	0.0	5.3
65	15.39	84.61	0.0	...
66	14.73	85.27	0.0	14.8
67	12.70	87.30	0.0	21.5
68	11.27	88.71	2.5	23.4
69	9.84	90.16	8.1	27.8
70	8.33	91.67	34.8	28.9
71	6.78	93.22	69.1	32.5
72	3.52	96.48	100.0	...
		Gravel		
93	8.22	91.78	0.0	....
94	6.13	93.87	2.4	....
95	5.53	94.47	7.0	....
96	4.70	95.30	20.3	....
97	3.90	96.10	47.0	....
98	2.12	97.88	60.0	....

However, the sharply rising part of the brittleness curves in reality rises considerably more abruptly. In other words, the brittleness numbers corresponding to the rising part of the curve are too low and the deviations from correct values are greater, the higher the brittleness.

Another important factor is the temperature. Just as the stability is determined at temperatures at which it is the lowest, so should the brittleness be determined at the lowest temperature which can be conveniently maintained in the laboratory. We have at present a small unit built to fit a 6 cubic foot (0.17 cubic meter) household refrigerator. However, since few laboratories are equipped with large refrigerators, the next best thing is to carry out the test at room temperature as low as possible and constant within 5° C. This requirement is obviously important if the results of different laboratories are to be compared. For each individual laboratory, however, the temperature is not as serious a factor as it seems, especially if the effect of the temperature is borne in mind; viz., at lower temperatures the abrupt change in brittleness occurs at somewhat higher asphalt content. Essentially, the effect of lower temperatures is to give a higher brittleness number of briquets which are appreciably brittle, even at room temperature—i. e., a brittleness above 2 per cent.

This fact is illustrated in the following table, where brittleness numbers of several mixtures obtained under different temperature conditions are given. In line one are given the brittleness numbers obtained with briquets kept and tested at room temperature (18–20° C.). In the second line are figures obtained at 30–33° C. In the third line are given brittleness numbers of similar briquets which were kept in the refrigerator for at least 24 hours and tumbled at 30–33° C. The effect is too small to change the nature of the brittleness curve essentially:

Aged and tested at 18–20° C.	1.6	1.2	20.6	66.0
Aged and tested at 30–33° C.	0.7	0.9	20.0	51.7
Aged in ice box and tested at 30–33° C.	1.2	0.9	25.5	62.1

Certain steam-refined asphalts, however, are extremely brittle at low temperatures, and prechilling in the ice box yields appreciably higher brittleness numbers.

### Stability Test

The Hubbard-Field stability test and some of the others measure the sum total of all forces which contribute to the strength of an asphalt mixture. These forces include those of plastic or viscous flow, the adhesive forces of the asphalt towards the aggregate, the tensile strength of the asphalt, the friction of the particles, and the mutual attraction of the particles of the mineral aggregates. That friction and interlacing of the aggregate are important factors contributing towards the stability is not difficult to conceive. Green and Haslam (7) showed that the yield value of pigment-vehicle mixtures involves the interfacial tension and the friction between the particles; Horsefield (8) supports the view that friction and interlacing of the particles of the aggregate determine the stability of asphaltic mixtures. That there is a force of mutual attraction of the solid particles acting through the film of asphalt is not improbable. That such molecular forces exert "a powerful influence on the molecules of the extremely thin liquid glue film" between surfaces of quartz and steel is postulated by Lee (14). That such molecular attraction exists is also supported by evidence obtained with joints between steel-steel and steel-copper surfaces. It is not unlikely that similar forces exist between the particles of an asphalt mixture.

Of all the factors contributing to the strength of a paving mixture, those most responsible for failure are the continuous flow and mobility (viscous or plastic) of the asphalt and the lowering of the frictional and interlocking resistance of the aggregate. It is desirable, therefore, to design a method which will measure the stability of a mixture involving these two factors only. The specimen should deform because of continuous flow or mobility, without rupturing the bond between the asphalt and the aggregate.

Such a test can be made with a plunger which covers only a fraction of the surface of the specimen, so that there is compression underneath and flow immediately adjacent to and around it (18). That such a plunger should have the geometry of a hyperbola of revolution, such that the rate of increase of the radius is proportional to the depth of penetration, is obvious. Unfortunately, hyperbolas of revolution are difficult to machine. As a practical alternative, spheres suggest themselves.

### Design and Procedure

How (9) was probably the first to use a ball penetration test, similar to the Brinell hardness test, for the determination of the stability of asphalt paving mixtures. Subsequently others used similar methods (16).

In the design of a sphere penetration method as a stability test, numerous details of construction are possible, but they are of little importance. The chief problem is the choice

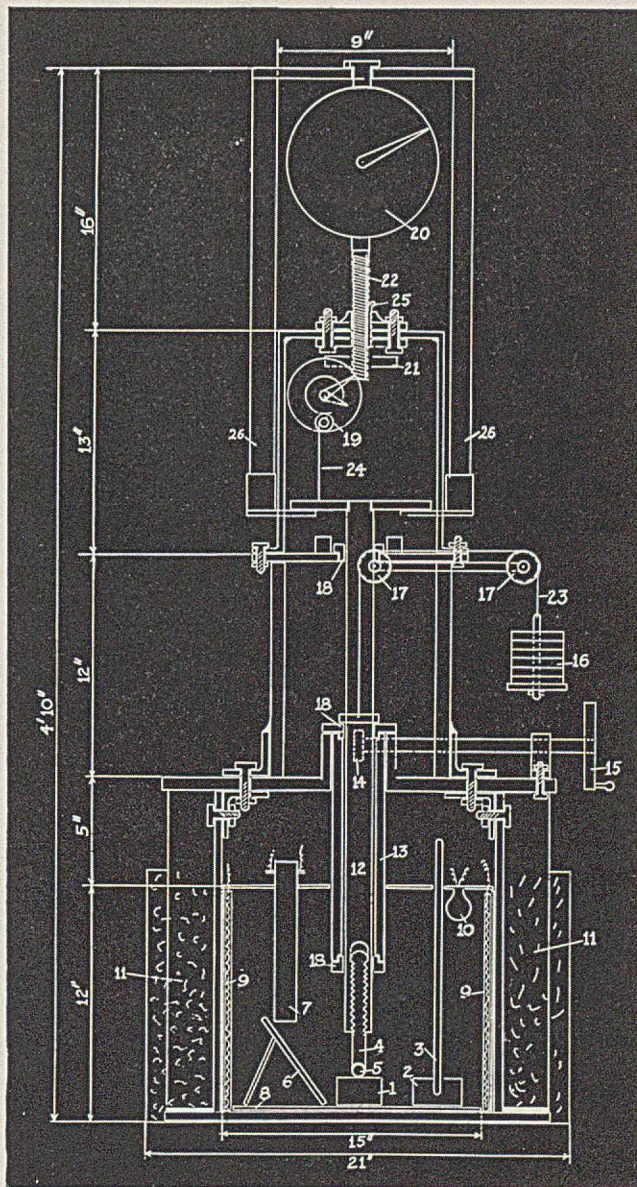


FIGURE 2. STABILITY TESTING DEVICE

1. Specimen to be tested
2. Block similar to specimen into which thermometer is embedded
3. Thermometer
4. Plunger
5. Sphere  $\frac{3}{4}$  inch in diameter
6. Mirror
7. Thermoregulator
8. Asbestos plate
9. Electric heaters
10. Pilot light
11. Asbestos fiber insulation, 4 inches thick, around thermostat
12. Vertical shaft, 1 inch in diameter
13. Concentric shaft used to raise shaft 12 and thus remove load from specimen when test is completed
14. Gear, serving to lift shaft 13, operated by:
15. Handwheel
16. Counterweight
17. Brass pulleys mounted on ball bearing, two on each side of shaft
18. Ball bearings
19. Micrometer
20. 200-pound (90.7-kg.) spring balance
21. Handwheel for applying load
22. Screw operated by 21
23. 22-gage nichrome wire
24. Silk string connecting micrometer to shaft 12
25. Key which keeps screw 22 from turning when load is applied
26. Standard 1-inch aluminum pipe

of the most suitable variables: (1) choice of the independent variable, time or load; (2) radius of the sphere to be used; (3) ultimate depth of penetration; (4) use of a confining mold or not; (5) dimensions of the specimen.

Any combination of these variables should yield interesting

results, some more so than others. The availability of so many combinations is an attractive feature for the research man.

The procedure adopted in the test to be described consists in increasing the load uniformly and intermittently at a rate of 3 pounds (1361 grams) per minute in steps of  $\frac{1}{2}$  pound (226.8 grams) every 10 seconds until a ball  $\frac{3}{4}$  inch (1.9 cm.) in diameter is depressed  $\frac{3}{8}$  inch (9.5 mm.) under the increasing load. The specimen, resting on a level plate, is not confined by a mold so that the pressure exerted by the sphere in radial directions is resisted by the material itself and not by a confining mold. The specimen is of the same dimensions as those used in the brittleness measurements— $6 \times 2\frac{1}{2} \times 1\frac{1}{2}$  inches ( $15.2 \times 6.4 \times 3.8$  cm.). Preliminary tests indicated that specimens larger than these did not change the results appreciably.

The ultimate load (in pounds) required for a depression of  $\frac{3}{8}$  inch is considered an index of the stability. However, weight is given to the performance of the specimen under the test—whether it cracked (C), broke (B), or yielded a perfect impression of the sphere without any visual signs of rupture.

This is the simplest representation suitable for control laboratories. For the research man, however, this test reveals a closer insight. Several different representations are possible; for example, the relation of the initial and final rates of deformation is of interest. A diagram of the apparatus is outlined in Figure 2. The air thermostat shown was subsequently replaced by a water bath, the temperature

of which was kept constant at  $60^\circ \text{C.} \pm 0.2^\circ$ . With a water bath closer checks are possible.

A specimen, which was allowed to reach temperature equilibrium for at least an hour, was placed under plunger 4, and sphere 5 was inserted in the space between. The plunger can be adjusted to accommodate specimens of different thicknesses and spheres of several different diameters. The plunger is lowered by means of handwheel 21, which operates spring balance 20, until micrometer 19 indicates that no downward movement results, while the weight on the spring balance increases to  $\frac{1}{2}$  pound. Vertical shaft 12 communicating the load to the sphere is counterbalanced by weight 16 so that a little less than  $\frac{1}{2}$  pound on the spring balance is needed to move it downward. The operation with an air thermostat is considerably simpler; contact of plunger and sphere is then indicated by mirror 6.

After contact is made, the load is increased in steps every 10 seconds and the reading of the micrometer recorded at regular intervals. When the micrometer indicates that the plunger has moved downward  $\frac{3}{8}$  inch, the test is stopped and the plunger is lifted by means of concentric shaft 13. The final reading on the balance is recorded as the stability. The specimen is then removed and its condition inspected. This visual inspection, however, is unnecessary; the operator can tell at any time during the test whether the specimen failed or remained sound throughout the test. If the readings of the micrometer are plotted against the corresponding loads, a permanent record is obtained which yields a correct representation of the performance of the specimen during the test. Such records can be made by a simple automatic recorder attached to the apparatus.

A few characteristic curves are shown in Figure 3, where the depth of penetration is plotted against the load. The curves are similar to those obtained by Emmons and Anderton (5) with their method of stability measurement which consists of compressing a specimen  $8 \times 6 \times 2\frac{1}{4}$  inches ( $20.3 \times 15.2 \times 5.7$  cm.) in a mold containing three extrusion openings. The load is applied by means of a 20,000-pound (9,072-kg.) compression machine through a plate with a clearance of  $\frac{1}{16}$  inch (1.6 mm.) around the sides of the mold. Loads corresponding to a displacement of 0.5 mm. are taken to represent the stability. The similarity of the curves is of interest only in so far as the objective which they wished to attain with their device is identical with the objective of this investigation—viz., "to cause an internal movement and rearrangement of the particles without leaving them free to dissociate themselves completely during the progress of the test." The objections to their method of testing are the bulkiness of the specimen (19) and the likelihood that slight variations in the mold dimensions will make large differences in the stability, as has proved to be the case in the Hubbard-Field test (17).

### Results of Tests

The data are given in Table III. Mixtures made with sands A, B, and C, containing variable quantities of limestone dust, and asphalt, are included. The stabilities (average of three tests) corresponding to pounds required to move the sphere downward  $\frac{3}{8}$  inch are given in column 5. Column 6 shows the corresponding percentage of voids in the compressed specimen, computed as described in the preceding section.

In Figures 4, 5, and 6 are plotted the brittleness numbers, the stability, and the percentage of voids against the percentage of asphalt by weight.

The most interesting feature of the stability curves is that a definite maximum is obtained. Also, this maximum corresponds with the lower portion of the rising part in the brittleness curve. When the proportion of asphalt is excessive or deficient, the stability is practically independent of the amount of filler, and the mixtures corresponding to the upper part of the knee in the brittleness curve, crack (C) or break (B) before the stability test is completed, or while it is in progress.

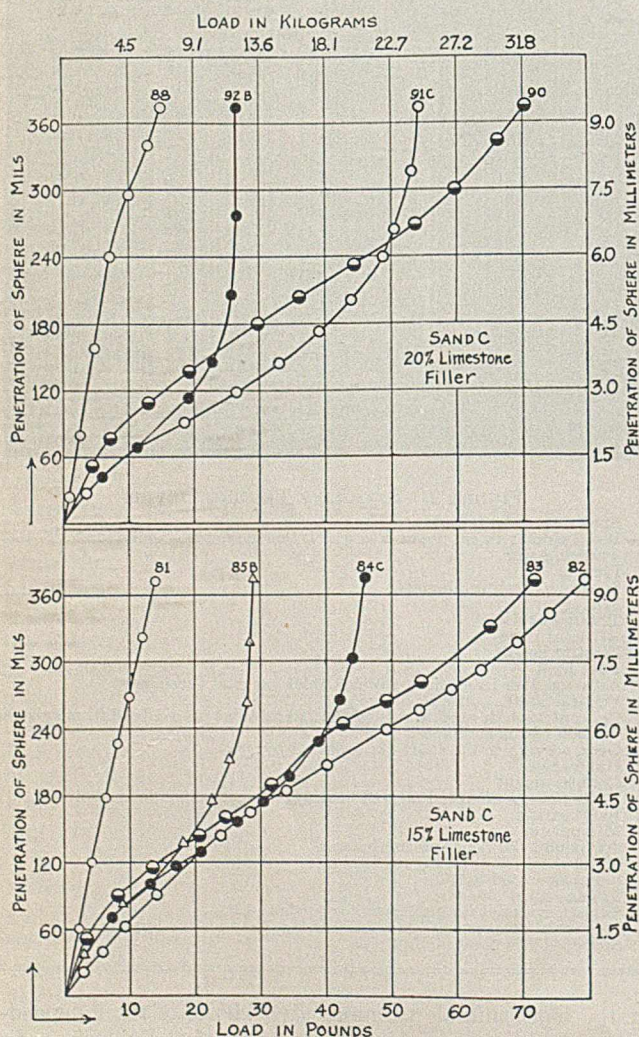


FIGURE 3. VARIATION OF DEPTH OF PENETRATION WITH LOAD

The number above each curve designates mixtures given in Table III.

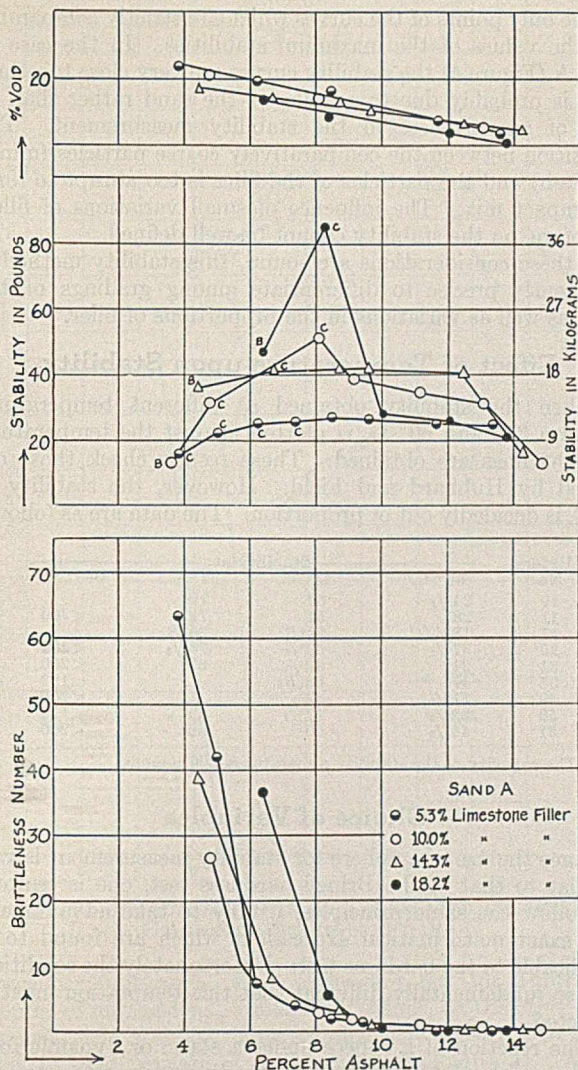


FIGURE 4. EFFECT OF FILLER ON CORRELATED PROPERTIES IN COMPACTED SPECIMEN OF SAND A

Highway engineers have recognized that, although the stability of mixtures carrying as much as 30 per cent of filler is high as determined by previous methods, the stability is greatly affected by slight variations in bitumen content, and that a mixture containing a proportion of filler somewhere between 10 and 20 per cent is most practical (18). The curves in Figure 6 prove this fact. The stability, as determined by the sphere penetration method, yields a lower value for 20 per cent filler content than for mixtures containing 15 per cent filler. Furthermore, if the maximum stabilities are plotted against the per cent filler, a break in the curve is noted at about 15 per cent filler. None of the other methods of measuring stability (as far as the writer knows) indicates these facts, although the practical highway engineer has learned to beware of high-filler, high-stability mixtures.

Figure 4 shows that a high-filler content may yield a sharply rising stability curve. The sphere penetration method indicates, however, that such stabilities are due to rigidity, since they are accompanied by cracking (C) before the test is completed—i. e., before the sphere has penetrated to a depth of half its diameter. Presumably, the value of an asphalt pavement is enhanced by its pliability. Rigidity is not desired even if the increased stability is advantageous. Furthermore, since such high-stability mixtures invariably lie within the danger zone of the brittleness curve, they cannot be considered as useful. This case demonstrates

graphically where a combination of the two tests described here yields an insight into the usefulness of a mixture which other methods fail to reveal.

The question may arise as to whether this method of stability determinations is sufficiently precise to indicate the optimum percentage filler to be used with a given sand. As shown in Figure 4 (sand A), the maximum stability is obtained at asphalt contents below that necessary to avoid excessive brittleness. Furthermore, the irregularities of the stability curves seem to indicate an experimental error of a

TABLE III. COMPOSITION, BRITTLENESS NUMBER, AND PERCENTAGE VOIDS IN COMPRESSED BRIQUETS

Mixture No.	Asphalt Aggregate		Brittle-ness No.	Stability		Voids %
	Per cent by weight			Pounds	Kg.	
Sand A, 5.3% Limestone Dust						
10	13.63	86.37	0.0	25.0	11.3	3.56
11	11.63	88.37	0.0	25.0	11.3	7.43
12	9.52	90.48	1.4	26.5	12.0	...
13	8.44	91.56	2.0	27.0	12.2	16.40
14	7.32	92.68	4.1	25.0(C) <sup>a</sup>	11.3	...
15	6.18	93.82	7.2	25.0(C)	11.3	19.36
16	5.00	95.00	42.3	22.0(C)	10.0	...
17	3.80	96.20	63.3	15.5(C)	7.0	24.11
Sand A, 10.0% Limestone Dust						
18	14.88	88.12	0.0	13.0	5.9	...
19	13.05	86.95	0.5	31.5	14.3	5.26
20	11.11	88.89	0.9	35.0	15.9	...
21	9.09	90.91	1.8	39.0	17.7	...
22	8.05	91.95	2.9	52.0(C)	23.6	14.54
23	4.76	95.24	26.6	31.5(C)	14.3	21.32
24	3.62	96.38	100.0	13.0(B)	5.9	23.24
Sand A, 14.3% Limestone Dust						
25	14.29	85.71	0.0	16.0	7.3	4.45
26	12.50	87.50	0.0	40.0	18.1	6.80
27	9.68	90.32	0.7	41.5	18.8	10.80
28	8.70	91.30	3.0	41.8	18.8	12.70
29	6.67	93.33	18.1	41.0(C)	18.6	14.80
30	4.45	95.55	38.6	36.0(B)	16.3	17.00
Sand A, 18.2% Limestone Dust						
31	13.73	86.27	0.0	21.0	9.5	0.10
32	12.00	88.00	0.0	26.0	11.8	3.72
33	10.00	90.00	0.4	27.5	12.5	...
34	8.33	91.67	5.6	85.0(C)	38.5	8.50
35	6.38	93.62	36.5	47.0(B)	21.3	13.08
Sand B, 7.0% Limestone Dust						
42	16.90	83.10	0.0	8.0	3.6	...
43	14.50	85.50	0.4	17.0	7.7	0.43
44	11.94	88.06	0.8	36.0	16.3	3.76
45	10.61	89.39	1.0	28.0	12.7	7.87
46	9.23	90.77	1.4	27.0	12.2	10.33
47	6.29	93.71	9.4	22.0(C)	10.0	15.44
48	3.39	96.61	44.1	29.0(B)	13.1	18.22
Sand B, 12.7% Limestone Dust						
49	16.00	84.00	0.0	17.0	7.7	...
50	13.70	86.30	0.0	22.5	10.2	0.34
51	11.26	88.74	0.0	44.5	20.2	2.35
52	10.00	90.00	0.7	42.0	19.1	3.12
53	8.70	91.30	1.0	40.5	18.4	6.54
54	6.00	94.00	13.8	35.0(C)	15.9	12.17
55	4.55	95.45	69.6	29.0(B)	13.1	15.65
Sand B, 18.0% Limestone Dust						
56	15.9	84.11	0.0	14.0	6.3	...
57	12.99	87.01	0.8	18.5	8.4	0.15
58	11.84	88.16	0.9	35.0	15.9	0.50
59	9.47	90.53	1.0	36.0	16.3	0.72
60	8.17	91.83	1.8	31.5	14.3	2.81
61	5.64	94.36	35.00	35.0(C)	15.9	9.27
62	4.00	96.00	100.00	18.0(B)	8.1	...
Sand C, 10.0% Limestone Dust						
73	20.00	80.00	0.0	15.0	6.8	...
74	16.67	83.33	0.3	45.0	20.4	1.74
75	13.10	86.90	0.5	70.0	31.7	7.26
76	11.11	88.89	0.8	55.0	24.9	13.20
77	9.09	90.91	1.0	39.0(C)	17.7	18.50
78	6.98	93.02	2.4	33.0(C)	15.0	23.21
79	4.77	95.23	84.9	19.0(B)	8.6	26.13
Sand C, 15.0% Limestone Dust						
80	20.00	80.00	0.0	10.0	4.5	...
81	16.67	83.33	0.5	14.5	6.5	2.62
82	13.10	86.90	0.6	83.0	37.6	3.32
83	11.11	88.89	0.9	67.0	30.4	10.98
84	9.09	90.91	1.2	48.0(C)	21.8	16.70
85	6.98	93.02	2.6	30.0(B)	13.6	21.43
86	4.77	95.23	91.9	19.0(B)	8.6	26.24
Sand C, 20.0% Limestone Dust						
87	20.00	80.00	0.0	15.0	6.8	2.86
88	16.67	83.33	0.7	16.0	7.3	2.84
89	13.10	86.90	0.8	73.0	33.1	2.94
90	11.11	88.89	0.9	67.0	30.4	6.62
91	9.09	90.91	1.5	54.0(B)	24.5	13.04
92	6.98	93.02	78.3	26.0(B)	16.3	19.13

<sup>a</sup> C = crack; B = break.

magnitude sometimes as great as the difference caused by variations of 5 per cent filler. The author feels justified in answering this question affirmatively.

In the first place, the sphere penetration stability method can be improved to yield considerably more precise data than the author was able to attain with his homemade apparatus. Again, the irregularities of the curves do not necessarily imply corresponding experimental errors.

In comparing properties of mixtures, it is essential to evaluate what are corresponding compositions. There is no correspondence between mixtures containing different proportions of filler but the same percentage of asphalt, when the relative proportions are expressed in weight relations. A much closer approximation to equivalence could be attained in terms of available percentage voids and total surface of the aggregate. A lengthy discussion on the relation between the percentage voids and the grading of the aggregate and proportion of filler is beyond the scope of this paper. It is easy to visualize, however, that the amount of asphalt needed to fill the voids and cover the surfaces of the aggregate at first decreases as more and more filler is added and finally begins to increase with excessive filler. Mixtures containing more asphalt than is needed to obtain this "saturation" point will exhibit approximately the same stability, regardless of the amount of filler. On the other hand, the proportion of filler determines the amount of asphalt necessary to attain this asphalt saturation point. In view of this qualitative consideration it is obvious that no parallelism among the stability curves can be expected. Furthermore, since the stability is a measure of two forces (resistance to vertical compression and lateral displacement), certain irregularities of the curves should be expected.

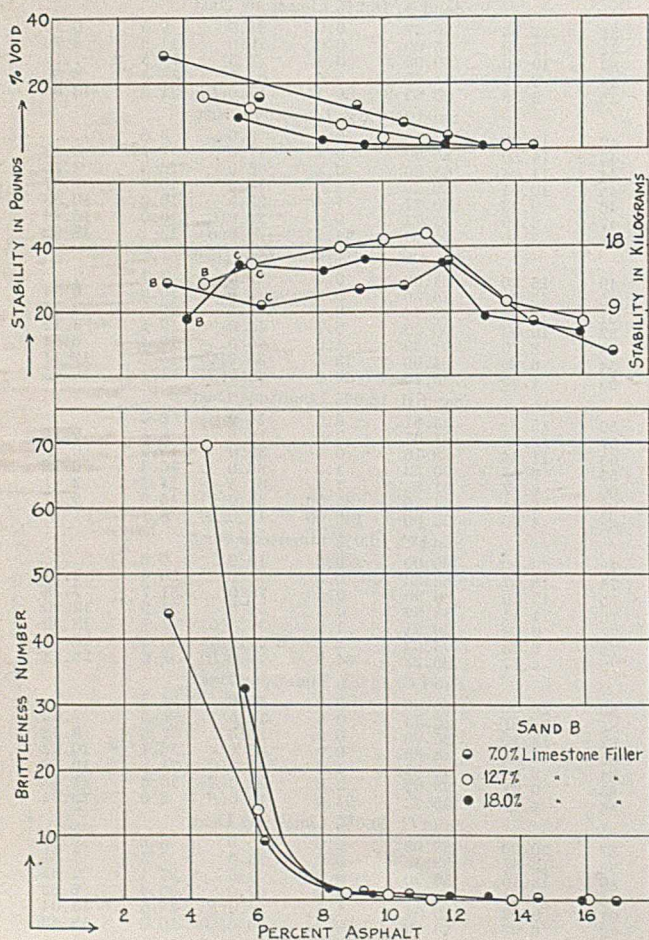


FIGURE 5. EFFECT OF FILLER ON CORRELATED PROPERTIES IN COMPACTED SPECIMEN OF SAND B

The only points of the curves which are strictly comparable are the values of the maximum stabilities. In the case of sand A (Figure 4) the stability curves are very close together. This is probably due to grading of the sand rather than to lack of sensitiveness in the stability measurement. The transition between the comparatively coarse particles (minus 50 mesh) and the particles of the filler is too abrupt to form a compact mix. The influence of small variations of filler, therefore, on the stability cannot be well defined.

If these considerations are sound, this stability method is sufficiently precise to differentiate among gradings of the sand as well as variations in the proportions of filler.

### Effect of Temperature upon Stability

When the stability obtained at different temperatures between 35° and 60° C. is plotted against the temperature, straight lines are obtained. These results check those obtained by Hubbard and Field. However, the stability at 0° C. is decidedly out of proportion. The data are as follows:

Mixture No.	Stability at:			
	60° C.	48° C.	37° C.	0-3° C. <sup>a</sup>
10	24½	59	79	...
11	28	51	73	<200
17	18½(C)	26(B)	25(B)	...
20	37½	59½	73½	<200
31	21	42½	65	<200
35	47	68(B)	...	182
49	21½	32	...	<200
50	22½	47½	69	175
51	44½	69	86	<200

<sup>a</sup> The capacity of the stability apparatus is 200 pounds.

### Choice of Variables

Since the use of a sphere for stability measurement is very similar to that of the Brinell hardness test, one is tempted to follow the same principles, if only to take advantage of the exact mathematical expressions which are found to be applicable to the hardness test. Unfortunately the conditions are so fundamentally different that this temptation must be rejected.

The reaction of a sphere under a static or dynamic force upon an elastic or semi-elastic body frequently manifests itself at an appreciable distance away from the point of contact. In the case of homogeneous molecular bodies, such as metals, the diameter of the impression made is a measure of its resistance, and the area of the spherical portion of the indentation is a measure of the distribution of force per unit area. The depth of the impression is important only in so far as it is geometrically related to the other two variables.

An asphalt paving mixture is not a homogeneous body. Its reaction to a sphere under static or dynamic forces is the resultant of several components. Initially the component is primarily compression. Then compression is associated with ductility or a pull which is conveyed to the surface at an appreciable distance from the ball. There is also the effect similar to that of a chain of elastic bodies under impact, which results in an elevation of the original surface of the briquet at a distance of several centimeters away from the point of contact of the sphere. The diameter of the actual spherical indentation, which in the Kreuger cell (2) is a measure of the elastic deformation of metals, cannot be accepted as a correct measure of the resultant reaction of asphaltic mixtures. Nor does the total distance the sphere was caused to move from its initial to its final position give a measure of the area of the surface of contact. The total distance is the sum of the depth of the spherical indentation plus the additional depth of a much larger diameter all around it.

Only in a few special cases, or when the total impression is only a small fraction of the radius of the sphere, can the distance indicated by the micrometer be considered a measure of the area of contact and, therefore, the distribution of



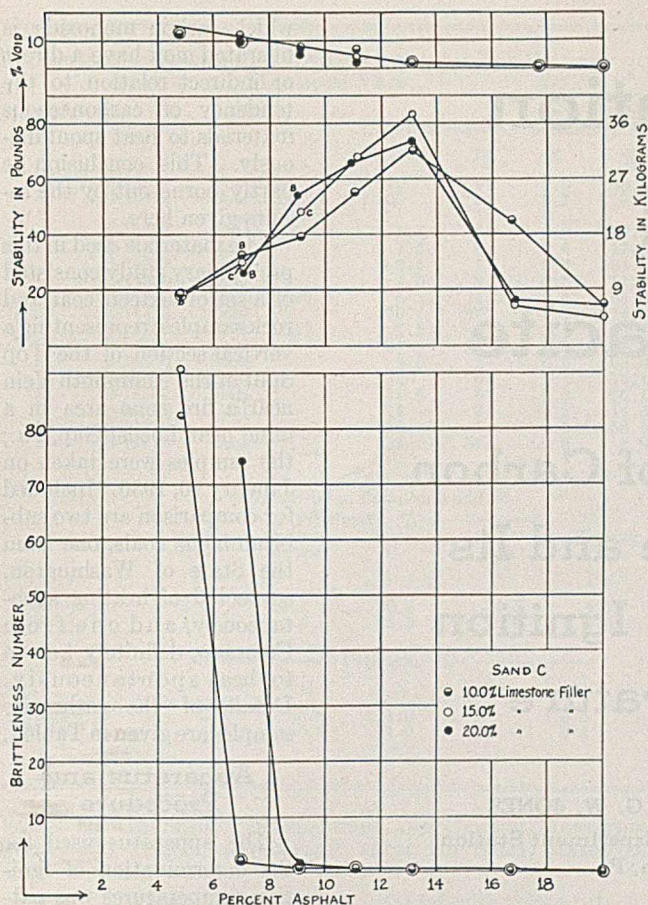


FIGURE 6. EFFECT OF FILLER ON CORRELATED PROPERTIES IN COMPACTED SPECIMEN OF SAND C

force per unit area. Such cases are few for appreciable depths of impressions. Small impressions, on the other hand, do not yield stability figures sufficiently sensitive to differentiate small variations in composition (Figure 3). Appreciable depth (that equal to the radius of the ball) was therefore chosen at a sacrifice of exact mathematical formulation.

In the case of large spheres the compression component is excessive for initial depths. A series of preliminary tests with spheres varying from  $1\frac{1}{2}$  to  $\frac{1}{4}$  inch (3.8 to 0.6 cm.) seemed to indicate that a  $\frac{3}{4}$ -inch (1.9-cm.) sphere is most satisfactory.

The time element is important. The procedure could be based on measuring the time necessary to move the ball downward to a given depth under a constant load. The choice of load, however, is not merely arbitrary, but the same load does not yield representative figures for different mixtures. It takes an appreciable period for a sphere to sink into a soft mixture even if the force is somewhat excessive. When the depth is plotted against the time for several constant loads, a family of similar curves is obtained. Any one of the curves could serve the purpose. Unfortunately, however, no clear-cut relation seems to exist between such curves obtained with a large variety of mixtures. It was thought best, therefore, to give the factors of time and load equal consideration, and increase the load in steps at equal time intervals.

It is not implied, however, that a better choice of variables could not be found nor that the choice of variables employed is free from arbitrariness.

### Conclusion

The procedure of design of asphaltic mixtures described consists first in determining the compositions of mixtures which

possess a brittleness number between 0 and 2. This establishes the minimum asphalt to be used with a given aggregate. These mixtures are then subjected to a stability test to determine which of these has the highest stability. This differentiates between kind of aggregate, asphalt, and proportion of filler to sand. If the brittleness is measured at higher room temperatures ( $30^{\circ}\text{C}.$ ), the range is reduced to 0-1.

The brittleness number is the percentage loss by weight after an hour of tumbling in a revolving drum.

The stability test consists of measuring the maximum load (in pounds) required to force a sphere  $\frac{3}{4}$  inch in diameter into the specimen to a depth equal to the radius ( $\frac{3}{8}$  inch). The load is applied in uniform steps at the rate of  $\frac{1}{2}$  pound every 10 seconds, and the temperature of the specimen is maintained at  $60^{\circ}\text{C.} \pm 0.2^{\circ}$ .

This procedure precludes the necessity for a priori knowledge of the service records of given mixtures in so far as the brittleness and the stability are concerned. The author realizes, however, that the design of a successful asphaltic paving mixture is exceedingly involved and that many factors are determined by neither the stability nor the brittleness. The ultimate test must be a large-scale road trial.

Yet the fact that these tests determine compositions which show low brittleness and high mobility under the heaviest load may guide the research man working with new asphalts or modified asphalts in deciding which of the compositions are best and help him to vary the constituents so as to obtain the best possible composition. The highway engineer, on the other hand, may decide by means of these tests whether a new mixture holds sufficient promise to justify large-scale trials.

The brittleness test alone establishes the minimum asphalt to be used, regardless of any other factors, by the simple expedient of plotting the brittleness numbers against the percent asphalt. The curve thus obtained indicates the dangerous zone of asphalt content.

The stability test, on the other hand, gives a maximum stability, not due to rigidity, establishing the best mixture in reference to suitable aggregate compositions.

The results given in demonstration of the procedure check closely the fundamental facts empirically established by highway engineers, both as to the most likely percentage of asphalt and filler.

The apparatus described can be improved in many respects. The fundamental principles involved, however, are sound, and the method is useful and reliable.

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**T**HE Bureau of Mines is conducting an investigation dealing with the causes, behavior, and control of anthracite mine fires. The question of spontaneous heating of anthracite has received some consideration as a possible cause. It is generally agreed that a high-grade screened anthracite does not heat spontaneously, even during long periods of storage. The carbonaceous materials (roof rock, coal, bone, slate, and timber) occurring underground in anthracite mines, however, vary in chemical composition; they also vary widely at times with respect to the accompanying mineral matter, both as to amount and composition and as to the degree of dispersion of this matter throughout the carbonaceous substance.

Keene, Turner, and Scott (2) showed that the "initial reaction temperature" of anthracites towards carbon dioxide varies inversely with the volatile content of the carbonaceous matter and inversely with the amount of accompanying mineral matter. A good correlation is shown between volatile content and initial reaction temperature, but not between initial reaction temperature and ash content. The chemical composition of the ash appears to have a considerable influence; those ashes high in oxides or carbonates of the more basic metals exert the greatest catalytic effect in lowering the initial reaction temperature.

To identify quickly for further study the most readily ignitable coals or other materials found in an anthracite mine, the apparatus shown in Figure 1 was built. It was designed for a study of the ignition temperature and the liberation of carbon monoxide during heating in a current of air at temperatures up to the ignition temperature of the coal or other substance.

Special emphasis is placed on the rate at which carbon monoxide was liberated when the carbonaceous materials were heated at a constant rate in the presence of air. The writers believe that the ignition temperature and rate at

# Oxidation of Anthracite

## Liberation of Carbon Monoxide and Its Relation to Ignition Temperature

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A method and apparatus are described for obtaining the relative rates of liberation of carbon monoxide from carbonaceous substances during heating and for determining the ignition temperatures at the same time. The tests were designed primarily to identify quickly the most readily ignitable coals or other materials found in an anthracite mine, and form a part of the Bureau of Mines' investigation into the causes, behavior, and control of anthracite mine fires. Special emphasis is placed on the rate at which carbon monoxide was liberated when the carbonaceous materials were heated at a constant rate in the presence of air. The initial temperature and rate at which carbon monoxide is liberated may have a direct or indirect relation to the tendency of carbonaceous materials to heat spontaneously.

which carbon monoxide is liberated may have a direct or indirect relation to the tendency of carbonaceous materials to heat spontaneously. This conclusion is partly borne out by the results given here.

The materials used in this preliminary study consisted of a set of sixteen coal and rock samples, representing a vertical section of the Top Split of the Mammoth Vein near a fire zone area in a mine near Locust Gap, Pa.; the samples were taken on January 10, 1936. Included for comparison are two sub-bituminous coals, one from the State of Washington, suspected of heating spontaneously, and one from Colorado, definitely known to heat spontaneously. Details of the anthracite samples are given in Table I.

### Apparatus and Procedure

The apparatus used for the determination of ignition temperatures was patterned after that described by Holmes and Davis (1) with the exception that a mechanical arrangement was used to decrease continuously the outside resistance in such a manner as to produce a uniform heating rate, giving a rate of temperature rise of approximately 6° C. per minute. Figure 1 illustrates the apparatus.

Temperatures were measured by means of a 22-gage, bare iron-constantan thermocouple and recorded on the odd points of an 8-point Leeds & Northrup Micromax recorder. The electromotive force developed by the combustion of the carbon monoxide in the Hopcalite cell of a carbon monoxide indicator (Mine Safety Appliances Company) was recorded directly on the even points of the same recorder.

The mechanical arrangement for producing a straight-line heating curve was as follows: A sliding contact

rheostat, with 46 cm. of adjustment travel, was fastened to an assembly frame and actuated by a 0.25-h. p. motor and two speed-reducing gears in series with a total speed reduction of 20,000 to 1. The brass cone on the end of the slow shaft of the second reducing gear wound up a heavy linen cord which pulled the sliding contact of the rheostat and thereby cut out resistance at a decreasing rate.

The large stopper, containing the three bell-shaped funnels, was placed in the top of the combustion tube. The thermocouple

TABLE I. DESCRIPTION OF SAMPLES FROM TOP SPLIT OF MAMMOTH VEIN

Sample No.	Lab. No.	Material	Thickness		Dry Sulfur %	Dry Ash %
			Cm.	In.		
1	B-14325	Top slate	10	4	2.0	86.7
2	B-14326	Coal (2.5-inch slate bands)	23	9	3.1	17.2
3	B-14327	Slate	2.5	1	0.3	72.5
4	B-14328	Coal	7.5	3	1.6	17.7
5	B-14329	Slate	2.5	1	0.3	84.4
6	B-14330	Coal	7.5	3	3.3	11.9
7	B-14331	Slate (bone)	4	1.5	0.4	55.6
8	B-14332	Coal	170	67	1.1	14.4
9	B-14333	Coal (dirty)	7.5	3	0.5	35.4
10	B-14334	Coal	61	24	0.6	8.7
11	B-14335	Slate	2.5	1	0.9	63.0
12	B-14336	Coal	15	6	1.1	14.1
13	B-14337	Slate	12.5	5	1.0	76.1
14	B-14338	Coal	18	7	4.3	14.3
15	B-14339	Slate	18	7	0.3	55.6
16	B-12473	Coal	137	54	0.6	6.0

Analyses<sup>a</sup> of Samples 9 and 16

	Proximate, %				Heating Value Cal.
	H <sub>2</sub> O	Volatile matter	Fixed C	Ash	
Sample 9	2.6	6.4	56.5	34.5	4972
Sample 16	1.2	4.6	88.3	5.9	7767

	Ultimate, %				
	H	C	N	O	S
Sample 9	2.3	55.8	1.0	5.9	0.5
Sample 16	2.8	86.5	1.0	3.2	0.6

<sup>a</sup> As received basis.

TABLE II. IGNITION TEMPERATURES AND CARBON MONOXIDE INFLECTION POINTS OF SAMPLES<sup>a</sup> FROM TOP SPLIT, MAMMOTH VEIN

Sample No.	Ignition Temp., <sup>b</sup> ° C.			CO Inflection Point, <sup>b</sup> ° C.		
	A	B	Difference	A	B	Difference
1	...	Did not ignite...	...	453	480	27
2	450	...	...	375	...	...
3	498	491	7	447	426	21
4	432	438	6	387	384	3
5	...	Did not ignite...	...	323	341	18
6	435	447	12	375	381	6
7	456	471	15	384	396	12
8	468	471	3	375	369	6
9	345	348	3	333	330	3
10	471	483	12	374	369	5
11	450	453	3	369	378	9
12	456	456	0	357	366	9
13	...	Did not ignite...	...	393	366	27
14	429	420	9	351	354	3
15	432	438	6	345	348	3
16	463	471	8	381	363	18

<sup>a</sup> 14 to 28 mesh, Tyler.

<sup>b</sup> A and B are duplicate determinations.

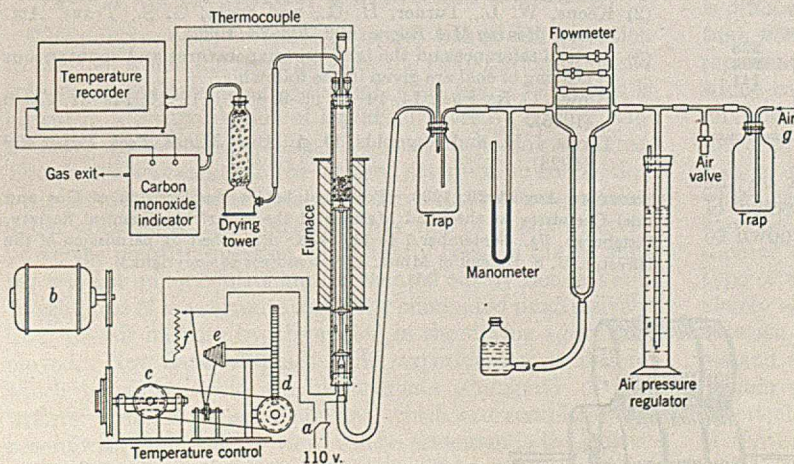


FIGURE 1. APPARATUS FOR STUDY OF CARBON MONOXIDE LIBERATION

leads passed through the outside funnels so that the position of the hot junction could be placed exactly on the grate. Rubber stoppers were then inserted and pressed into the tops of the funnels until practically air-tight. Seventy-five cubic centimeters of sample (14 to 28 mesh) were then poured through the larger center funnel, and the opening was closed with a rubber stopper. The temperature recorder motor was then started, the pump motor of the carbon monoxide indicator unit started, and the pump valve adjusted until the flowmeter indicated a rate of air flow equal to 3.3 liters per minute (7 cubic feet per hour). The carbon monoxide indicator contained an ammeter for showing the percentage of carbon monoxide directly. The needle was

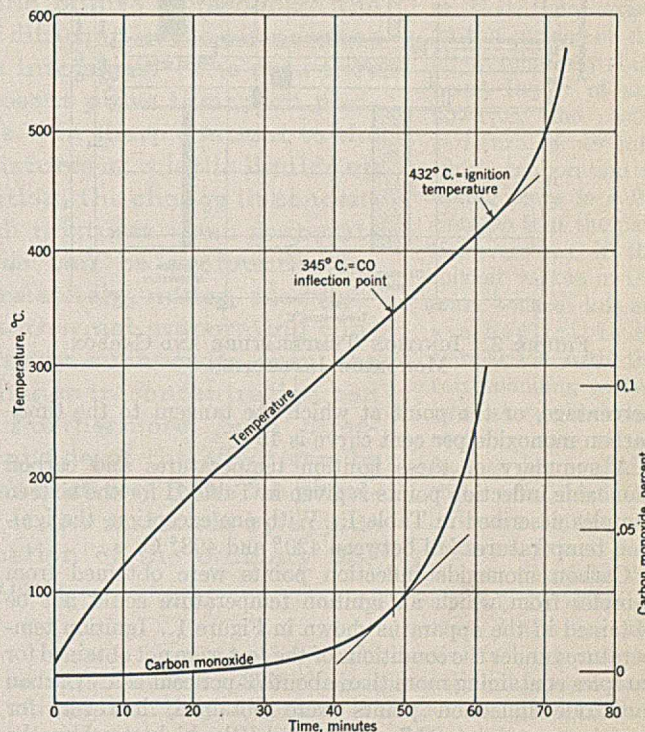


FIGURE 2. RECORDER CHART FOR SAMPLE 15 (14 TO 28 MESH)

actuated by the current from a series of thermocouples, whose hot junctions were embedded in the active compartment and whose cold junctions were embedded in the inactive compartment of the Hopcalite cell. The terminals of the thermocouple series were connected directly to the even points of the recorder and the percentage of carbon monoxide was obtained directly from the chart without the necessity of taking readings on the indicator. When the carbon monoxide line became constant, heater switch *a* was turned on; and motor *b* driving the reducing gears, *c* and *d*, and cone *e* controlling the outside resistance, *f*, was started. When the upper limit of the carbon monoxide indicator was reached (i. e., 0.1 per cent carbon monoxide), this instrument was disconnected from the circuit as follows: The pump motor was stopped, and air line *g* was turned on and adjusted, if necessary, to the rate of 3.3 liters per minute. A test was concluded when the temperature reached 600° C.

Results of Tests

Figure 2 illustrates a typical test, redrawn from the recorder chart so as to make time the abscissa and temperature the ordinate. The carbon monoxide percentages are shown on the same chart.

The ignition temperature is considered to be that point at which the time-temperature curve begins to depart from the straight-line heating curve, and is so indicated on Figure 2. The carbon monoxide inflection is that point at which the carbon monoxide content of the gases from the fuel bed changes from a slowly increasing to a rapidly increasing

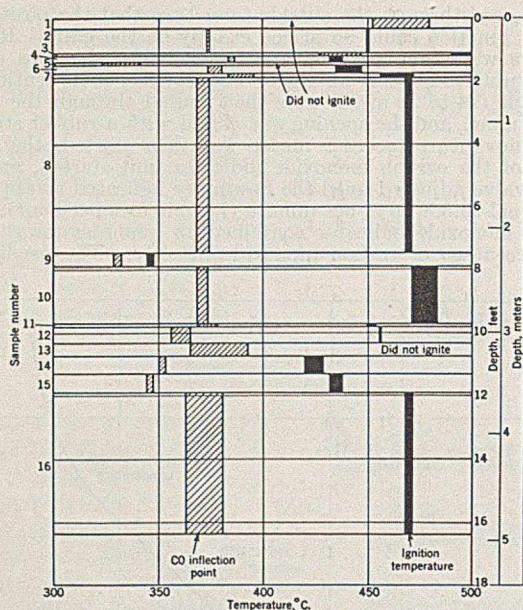


FIGURE 3. IGNITION TEMPERATURE AND CARBON MONOXIDE INFLECTION

percentage, or the point at which the tangent to the time-carbon monoxide per cent curve is  $45^\circ$ .

A summary of these ignition temperatures and carbon monoxide inflection points is given in Table II for the sixteen samples described in Table I. With one exception, the ignition temperatures fall between  $420^\circ$  and  $498^\circ$  C.

Carbon monoxide inflection points were obtained from samples from which an ignition temperature could not be obtained in the apparatus shown in Figure 1. Ignition temperatures under the conditions of the test were not obtained for samples containing more than about 73 per cent ash. Carbon monoxide inflection points were obtained, however, for samples containing 86.7 per cent ash (the highest ash in the group). Of the sixteen samples, No. 9 shows the lowest ignition temperature and the lowest carbon monoxide inflection point, and therefore may be the most susceptible of this group to heating spontaneously. Figure 3 gives the data of Tables I and II in graphic form.

TABLE III. IGNITION TEMPERATURES AND CARBON MONOXIDE INFLECTION POINTS OF SELECTED SAMPLES<sup>a</sup>

Sample	Ignition Temp., °C.	CO Inflection Point, °C.
Av. for anthracite samples	451	376
Most readily ignitable anthracite	346	331
Washington coals suspected of heating spontaneously:		
A	291	228
B	234	204
Colo. coal known to heat spontaneously	186	141
<sup>a</sup> 14 to 28 mesh, Tyler.		

Table III shows a comparison between the data on the anthracite samples, two subbituminous coals suspected of heating spontaneously, and a subbituminous coal known to heat spontaneously.

Table IV shows the effect of coal size and of moist and dry air on the ignition temperature and carbon monoxide inflection point.

TABLE IV. EFFECT OF SCREEN SIZE OF COAL AND OF DRIED AIR ON IGNITION TEMPERATURE AND CARBON MONOXIDE INFLECTION POINT OF SAMPLE 16

Size	Atmospheric Air		Dried Air	
	Ignition temp., °C.	CO inflection point, °C.	Ignition temp., °C.	CO inflection point, °C.
4 to 8 mesh:				
A	495	432	...	...
B	501	414	...	...
8 to 14 mesh:				
A	462	387	495	402
B	486	393	480	402
14 to 28 mesh:				
A	468	381	...	...
B	471	363	...	...

Figure 4 shows the content of carbon monoxide in the gases given off during heating in air by two anthracites, and by the three subbituminous coals previously mentioned.

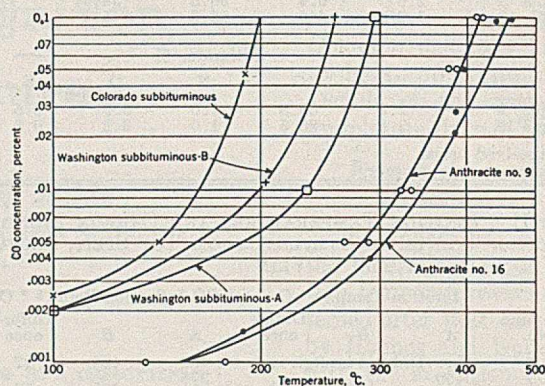


FIGURE 4. CONCENTRATION OF CARBON MONOXIDE IN GASES FROM DIFFERENT COALS

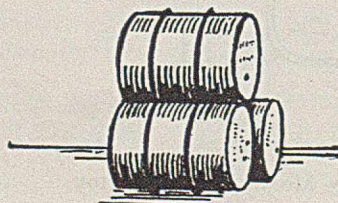
### Acknowledgment

The writers acknowledge the cooperation of J. D. Davis and C. R. Holmes who kindly loaned them their ignition temperature equipment until such time as the one described could be built. The samples of materials used in this work were analyzed by the Coal Analysis Laboratory under the direction of H. M. Cooper, and the carbon monoxide indicator was calibrated by L. B. Berger of the Gas Section.

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# Evaporation of Mixed Lacquer Solvents

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THE writers recently published an article (6) asserting "the assumption, hitherto made, that a solvent mixture of constant boiling point at the drying temperature of the film is a constant-evaporating mixture is, in general, false and likely to be grossly misleading." Bennett and Wright (1) have taken emphatic exception to this conclusion. They state that the writers express or imply three concepts: "(1) Evaporations of binary mixtures in closed vessels follow a special mechanism different from the simple process of distillation; (2) constant-evaporating solutions at the temperatures at which lacquer films dry do not follow the simple process of distillation for azeotropic mixtures; and (3) mixtures which are constant boiling at one temperature are not constant evaporating at the same temperature but under somewhat greater pressures."

The purpose of this paper is to refute their position, to point out the errors on which it is apparently based, and to establish firmly the theoretical and experimental correctness of the concepts quoted. (The writers believe that the restriction of a closed vessel was neither expressed nor implied in their paper.)

## I. Constant-Evaporating Mixtures Are Not, in General, Constant Boiling

The purpose of the original paper (6) was to call attention to the role which diffusion plays in the evaporation of mixed solvents in the presence of a diluent, inert gas, a role which is absent in the vaporization of liquid mixtures by boiling, particularly where one is dealing with constant-boiling mixtures. This factor was called to the writers' attention in connection with certain measurements on mixed solvent evaporation under conditions that certainly were not of a character to prove the point in question, particularly because the air supply was not under control and, as pointed out by Bennett and Wright, one of the solvents was being eliminated progressively from the air mixture by absorption in the drying agent employed. New data, obtained under experimental conditions which carefully avoid the unfortunate ambiguity of the writers' previous experiments and which are completely in accord with their point of view, will be presented in this paper.

The following is the position of the writers: A common condition under which solvent vapors evaporate from a lacquer

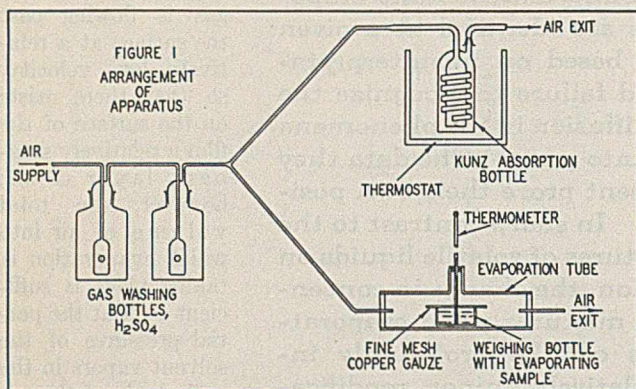
The contention of Bennett and Wright that constant-boiling and constant-evaporating mixtures are identical at a given temperature is based on misinterpretation of data and failure to recognize the significance of diffusion in the phenomena of evaporation into a gas. The data they themselves present prove their own position untenable. In sharp contrast to the behavior of mixtures of volatile liquids on simple distillation, the change in concentration of such mixtures when evaporating into a gas can be profoundly influenced by relatively minor modifications of the isothermal evaporating conditions. In many such cases even the direction of change in concentration can be reversed. Furthermore, both direction and magnitude of the effect can be calculated quantitatively from the physical constants of the materials by appropriate modification of the ordinary distillation equations.

surface of the lacquer and in a sense insulating it from contact with the main body of the air. This movement must follow the ordinary laws of diffusion. When the two constituents of a solvent have different diffusion rates, their diffusional velocities out from the lacquer surface into the air will differ correspondingly, and the process of evaporation will be modified thereby. This type of evaporation will be called "diffusional evaporation." The position of Bennett and Wright is equivalent either to denying that diffusion plays a part in the process or else to insisting that the diffusional characteristics of all the vapor constituents are identical. The decision must depend upon the facts.

Meanwhile, emphasis must be laid upon the fact that the evaporative conditions just described, while frequently encountered, are special, corresponding to a limiting case which is often closely approached though never truly reached in actual work. The other extreme of evaporating behavior is represented by any conditions which will bring all the air which carries the vapor away from the surface of the liquid mixture into equilibrium with the whole of the liquid. This, too, represents a limiting condition, perhaps even more difficult to realize experimentally than the preceding, but one which can be approximated by bubbling the air through the liquid in such a way as to ensure maximum interfacial surface, time of contact, and convection mixing of the liquid. This type of evaporation of mixed solvents into a gas would completely eliminate diffusion as a factor influencing the relation between change in composition of the liquid during the process and the amount of evaporation. It will be called "equilibrium evaporation" but is rarely if ever approximated in practical lacquer work. Except for the effect of the presence of the inert gas on solvent equilibrium between liquid and vapor, an effect which is usually negligible under practical conditions, evaporation of this type would be fully equivalent

film is one in which the air or other inert gas is flowing past the surface at a relatively low velocity, so that there exists on the surface of the film a relatively stagnant layer of air; however, the total volume of air into which evaporation is taking place is sufficient so that the partial pressures of the solvent vapors in the main body of this air are negligible in comparison with the corresponding partial pressures existing at the surface of the lacquer film. Under these conditions the solvent vapors can escape from the lacquer film into the air only by diffusion through the so-called air film blanketing the

to ordinary distillation by ebullition and, as far as changes in composition of the mixture with evaporation are concerned, follows the same laws. It must be emphasized that in the statements of their previous article the writers were considering only diffusional evaporation or conditions in which diffusion is a significant factor.



Visualize a binary, constant-boiling mixture evaporating into air. The vapor at the interface between liquid and gas will be in substantial equilibrium with the liquid. Assuming conditions of diffusional evaporation, if the vapor constituents have identical diffusion velocities, they will diffuse away from the interface into the air at velocities proportional to their partial pressures, and therefore proportional to their mole fractions at the interface. Consequently, the mixed vapor at the interface will have the same composition as the liquid left behind, and the constant-boiling mixture will behave as a constant-evaporating mixture. If, however, one of the vapor constituents diffuses more rapidly than the other, its rate of diffusion away from the interface, relative to that of the other constituent, will be greater than the ratio of their partial pressures at the interface. Therefore the vapor evolved into the main body of the inert gas will be richer in the rapidly diffusing constituent than the liquid from which it came. Hence, the composition of the liquid will change during evaporation, and the constant-boiling mixture will no longer be a constant-evaporating mixture. Since relative vapor diffusion rates are dictated largely by molecular weight, one will in general expect the constituent of lower molecular weight to evaporate selectively, in this sense. Clearly,

it may be possible to have a liquid mixture of the two constituents in which the vapor pressure of the rapidly diffusing component relative to that of the other will be just enough to compensate for its higher relative diffusional velocity. Under conditions of diffusional evaporation, such a mixture will be a constant-evaporating mixture. The quantitative influence of volatilities and diffusivities in determining constant-evaporating composition will be discussed later in the paper.

It may be well to reiterate the point that, just as boiling any mixture of two solvents which has a constant-boiling composition of minimum boiling point tends to leave behind a liquid residue farther removed from the constant-boiling mixture than the original composition, so evaporation under

diffusional conditions of such a mixture possessing a constant-evaporating composition likewise tends to leave a residue progressively farther from that composition.

### Available Data and Their Significance

Bennett and Wright quote figures on ethanol-toluene which, if taken at face value, contradict the writers' position. They claim, as shown in their Table II, that the constant-boiling mixture and the constant-evaporating mixture are identical at any given temperature. However, we must keep in mind that the second column of their table—i. e., their figures on the compositions of the constant-boiling mixtures—is made up, not of data, but merely of their interpretation of

TABLE A. ISOTHERMS FOR SYSTEM TOLUENE-ETHANOL (10)

Mole Fraction Toluene Liquid $x$	Mole Fraction Toluene Vapor $y$	Total Pressure, Mm.	Mole Fraction Toluene Liquid $x$	Mole Fraction Toluene Vapor $y$	Total Pressure, Mm.
At 75° C.					
0.274	0.232	722	0.274	0.248	486
0.233	0.217	724	0.233	0.234	487
0.155	0.180	724	0.156	0.192	488
0.096	0.135	716	0.096	0.143	480
At 70° C.					
0.274	0.240	592	0.375	0.277	390
0.233	0.226	598	0.274	0.256	395
0.155	0.186	598	0.233	0.242	397
0.096	0.139	591	0.155	0.198	397
			0.096	0.147	388

the data of Wright (10). The writers believe Bennett and Wright were in error in estimating the constant-boiling mixtures from Wright's data (10) on the vapor-liquid equilibria of toluene-ethanol solutions. That this misinterpretation of the data of Wright is serious can be seen—e. g., by study of his figures at 60° C., his lowest experimental temperature, the essential points of which are shown in Table A condensed from his paper. At low values of  $x$  (mole fraction of toluene in the liquid), the corresponding values of  $y$  (mole fraction of toluene in the vapor) are higher than  $x$ , whereas at high values of  $x$  the reverse is true. At his experimental value of  $x = 0.233$ , his value of  $y$  is 0.242. In other words, the composition of the constant-boiling mixture must be greater than 0.242. Similarly, it must be less than 0.256, the value of  $y$  for his lowest liquid composition, 0.274, showing vapor composition lower than itself. Cross interpolation gives the constant boiling mixture as 0.247. Bennett and Wright's value, shown in their Table II on which they base their case, is 0.200, 20 mole per cent toluene. Table B, which is restricted to temperatures at which experimental data are given, shows the comparison of the compositions of the constant-boiling mixtures quoted by Bennett and Wright with those calculated from Wright's own data as just described. The errors of Bennett and Wright increase progressively as the temperature decreases. Extrapolating Wright's data either linearly

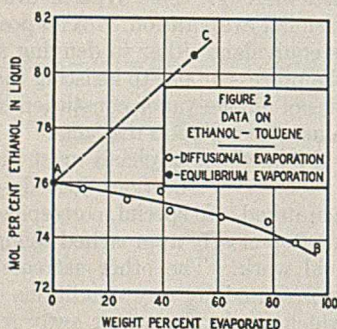


TABLE B. COMPARISON OF CONSTANT-BOILING COMPOSITIONS FOR TOLUENE-ETHANOL CALCULATED FROM VAPOR-LIQUID EQUILIBRIA DATA OF WRIGHT (10)

Temp. ° C.	Mole % Toluene	
	Calcd. by Bennett and Wright (1)	Calcd. by Authors
75	18.0	20.2
70	18.5	21.9
65	19.5	23.4
60	20.0	24.7

or by the extrapolation of his partial pressure curves indicates a constant-boiling mixture of approximately 35 mole per cent toluene at 25° C., as compared with 26.9 per cent for the constant-evaporating mixture reported by Bennett and Wright.<sup>1</sup>

### Experimental Data on Ethanol-Toluene

The conclusion seems inescapable that the data on ethanol-toluene mixtures presented by Bennett and Wright and by Wright, far from proving the identity of the constant-boiling and constant-evaporating mixtures are, on the contrary, proof of the falsity of "the assumption, hitherto made, that a solvent mixture of constant boiling point at the drying temperature of the film is a constant-evaporating mixture." Furthermore, the differences between the compositions of the two mixtures which their data show are in all cases in exactly the direction predicted by the assumption that diffusion is a significant factor in the evaporation. However, because the description of their conditions of evaporation was too meager to make sure that diffusion was the controlling factor, it seemed wise to check this point experimentally:

Mixtures of ethanol and toluene were exposed to evaporation under two sets of conditions approximating diffusional and equilibrium evaporation, respectively. In the first, the mixture was placed in a small weighing bottle, 20 mm. in diameter and 25 mm. high. To suppress eddy currents in the immediate neighborhood of the surface of evaporation, a fine-mesh copper screen was placed over the top of the bottle during the period of evaporation. The weighing bottle was placed upright in a horizontal 42-mm. glass tube, through which a stream of air, dried by bubbling through concentrated sulfuric acid, was passed at a rate of approximately 2 liters per minute. A thermometer was inserted through the top of the 42-mm. tube and extended into the liquid to measure the temperature of evaporation. The small error introduced by liquid hold-up on the thermometer bulb was ignored. The air was discharged through a small-bore tube to prevent back diffusion of moisture. In no case did the temperature of evaporation differ by more than 3° from 25° C. In the second set of conditions each sample was evaporated by placing about 12 cc. of mixture in a Kunz absorption bottle, immersed in a thermostat held at 25° C. Air taken from the same source as in the first experiment was slowly bubbled through the absorption bottle, the conditions assuring approximation to equilibrium. From time to time the loss in weight of the two bottles was determined, both bottles being carefully stoppered during weighing to prevent evaporation and contamination with atmospheric moisture, and small samples were removed for determination of concentration by measuring refractive indices at 25° C. The arrangement of the apparatus is shown in Figure 1. The toluene was Eastman's product of 1° C. boiling range and sulfur-free, and the ethanol was furnished through the courtesy of the Department of Chemistry of this institute and contained not over 0.2 per cent water.

The composition of the constant-evaporating mixture under diffusional conditions was determined by the usual technic (except for the precautions just described for assuring diffusional conditions of evaporation). The constant-evaporating mixture was found to contain 81 mole per cent ethanol; such a mixture showed no measurable change in composition after evaporation of 44 per cent by weight. The composition of the equilibrium evaporating mixture as determined in the Kunz absorption bottle was approximately 67.7 mole per cent ethanol (an initial mixture containing 67.5 per cent fell to 67.1 per cent after evaporation of 60 per cent by weight). The performance of a 76 mole per cent ethanol mixture under conditions of diffusional evaporation (curve AB) and of equilibrium evaporation (curve AC) is shown in Figure 2. The ethanol-toluene mixture behaves exactly as one would predict from the diffusional concept. Under conditions of diffusional evaporation, the composition of the liquid pro-

<sup>1</sup> It is not clear how Bennett and Wright made this serious error in interpreting Wright's data. Perhaps they tried to estimate the maximum of the total pressure curve. The flatness of this curve renders this method highly unreliable. Thus, Wright's data indicate that at each of the temperatures in question the pressure corresponding to the constant-boiling mixture as determined by the vapor-liquid composition data is never more than 1 mm. below the maximum pressure measured, the lowest value of which was 297 mm. The  $x$ - $y$  curve, on the other hand, crosses the diagonal of the  $x$ - $y$  plot at a considerable angle, and the point of intersection is easily determined. Certainly this method is far more precise than any based on the total pressure data.

gressively fell in ethanol content, the rate of change in concentration increasing progressively as evaporation went on. The sample of the same identical liquid submitted to conditions of equilibrium evaporation at the same temperature rose in ethanol content.

In other words, an initial mixture whose composition lies between the constant-boiling and constant-evaporating mixtures not only changes in composition on evaporation, but the direction of change can be controlled at will by the choice of the conditions of evaporation.

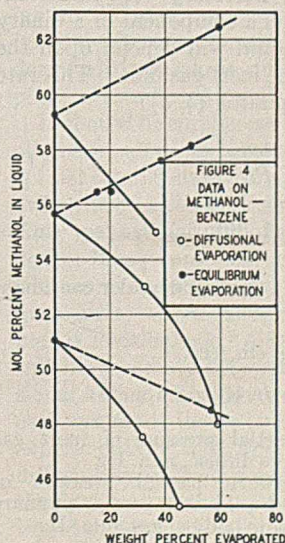
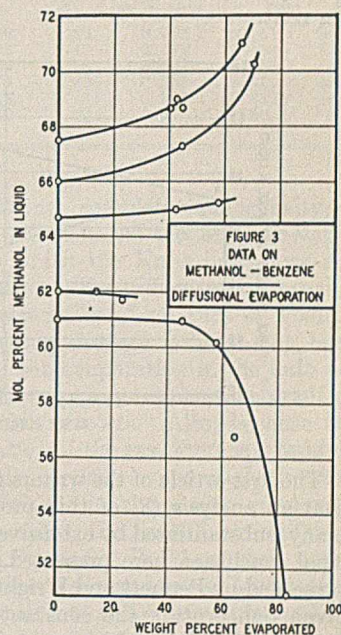
These facts, which are completely consistent with the diffusional concepts outlined above, are inexplicable on the assumption that a "constant-evaporating solution at the temperatures at which lacquer films dry. . . follows the simple process of distillation of azeotropic mixtures."

Bennett and Wright's experimental determination of the constant-evaporating mixture (26.9 mole per cent toluene at 25° C.) lies between the constant-evaporating composition as determined under diffusional conditions, 19 per cent, and the equilibrium evaporating mixture of about 32 per cent. This is almost certainly due to their maintenance of evaporating conditions intermediate between those of diffusional and of equilibrium evaporation, although the precise conditions are not clear from their article.

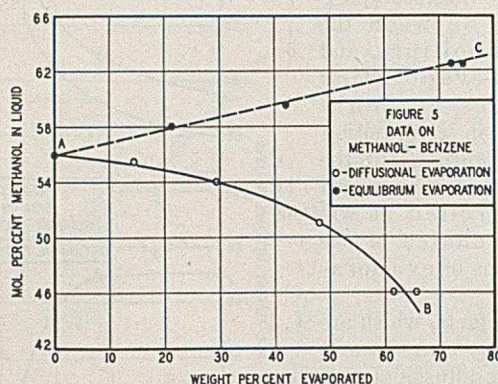
### Data on Methanol-Benzene

The writers have available data on methanol-benzene mixtures, collected in the apparatus and by the technic described above, which are more extensive and therefore even more convincing. The data for estimating the composition of the constant-evaporating mixture under diffusional conditions at 25° C. are shown in Figure 3, indicating that it contains about 64 mole per cent methanol. Figure 4 shows data on three mixtures, all initially below the constant-evaporating concentration; diffusional evaporation results are indicated by full and equilibrium evaporation by dotted lines. More detailed results on a mixture initially 56 mole per cent methanol appear in Figure 5. All these mixtures fall in methanol content under diffusional evaporation.

Furthermore, all but one of them fall through the constant-boiling mixture of approximately 51 per cent methanol (6). Under equilibrium evaporation, however, three of the four



initial mixtures rise in methanol content, only the mixture starting initially at the constant-boiling mixture falling less than 3 per cent when 55 per cent of it had evaporated. These data indicate a constant-evaporating composition under the equilibrium conditions of the Kunz bottle of about 53 per cent.



The first article of the writers (6) appeared the same month that an analysis (8) of this problem was published in Germany, substantiated by extensive data, and leading to the principal conclusion here presented. The data, including those presented by Bennett and Wright, prove inescapably that at a given temperature the constant-boiling mixture of two solvents can be changed in composition profoundly by evaporation into a gas under conditions where vapor diffusion plays a significant part (as is generally the case in drying of lacquer films); that the constant-boiling and constant-evaporating compositions are not in general identical; that relatively minor modification of the conditions of evaporation can profoundly change and even reverse the relative rates of vaporization of the components of a given mixture; and that the direction of all these effects can be foreseen and the results of modification of conditions predicted by taking into consideration the necessity of diffusion of the solvent vapors into the gas and the known diffusional characteristics and volatilities of the constituents.

## II. Theoretical Analysis

Granting that the conditions necessary for diffusional evaporation exist, the rate at which a component of a binary mixture leaves the body of the liquid will depend upon the rate at which it diffuses through the inert gas film. This rate is given by the Stefan diffusion equation (4, 5):

$$-\frac{dn_1}{d\theta} = \frac{D_1\pi}{RTX} \frac{\Delta p_1}{P_i} \quad (1)$$

where

- $-\frac{dn_1}{d\theta}$  = moles of component 1 diffusing/sec./sq. cm. of interfacial surface
- $n_1$  = moles of component 1 in liquid under consideration
- $\theta$  = time, sec.
- $D_1$  = diffusion constant, sq. cm./sec.
- $\pi$  = total pressure, atm.
- $R$  = gas constant, cc. atm./° K./gram mole
- $T$  = abs. temp., ° K.
- $P_i$  = logarithmic mean partial pressure of inert gas through which vapors diffuse, mm. Hg
- $\Delta p_1$  = mean difference between partial pressure of component 1 over liquid and partial pressure of component 1 in main body of gas, mm. Hg
- $X$  = film thickness, cm.

A similar expression holds for component 2:

$$-\frac{dn_2}{d\theta} = \frac{D_2\pi}{RTX} \frac{\Delta p_2}{P_i} \quad (2)$$

Dividing Equation 1 by Equation 2, and assuming that the partial pressures of both components are negligible in the main body of the gas in comparison with  $p_1$  and  $p_2$ , the vapor pressures of the components in equilibrium with the liquid, so that  $\Delta p_1 = p_1$  and  $\Delta p_2 = p_2$ , gives

$$\frac{dn_1}{dn_2} = \frac{D_1 p_1}{D_2 p_2} \quad (3)$$

From the definition of the relative volatility,

$$\alpha = \frac{y}{(1-y)} \frac{(1-x)}{x} = \frac{p_1 n_2}{p_2 n_1} \quad (4)$$

Equation 3 is equivalent to

$$\frac{d \ln n_1}{d \ln n_2} = \alpha D_1/D_2 \quad (5)$$

Equation 5 states that under conditions of diffusional evaporation the ratio of the fractional rates of change of  $n_1$  and  $n_2$  is equal to the product of the relative volatility into the ratio of the diffusion constants—i. e., the relative diffusivity. It will be noted that this is the familiar Rayleigh equation for simple distillation,  $d \ln n_1/d \ln n_2 = \alpha$ , except that the right-hand side,  $\alpha$ , has been multiplied by the ratio of the diffusivities,  $D_1/D_2$ .

When the relative volatility is equal to the reciprocal of the relative diffusivity, the right-hand member of Equation 5 is unity and therefore

$$\frac{dn_1}{dn_2} = \frac{n_1}{n_2} \quad (6)$$

Hence the composition of the net vapor actually evolved equals the composition of the liquid; i. e., the mixture does not change composition during evaporation. Therefore, it follows that the relation

$$\alpha = D_2/D_1 \quad (7)$$

is the condition for a constant-evaporating mixture under diffusional conditions, with negligible back pressure of solvent vapors. Furthermore, only when  $D_1/D_2$  is equal to unity will the constant-boiling and constant-evaporating compositions be the same.

For any mixtures, however complex, to evaporate without change in composition under diffusional conditions, the rates of evaporation of all components must be proportional to their concentrations. For a mixture of  $k$  components, this reduces to

$$\frac{D_1}{D_2} = \frac{1}{\alpha_{12}}, \quad \frac{D_2}{D_3} = \frac{1}{\alpha_{23}}, \quad \dots \dots \frac{D_{k-1}}{D_k} = \frac{1}{\alpha_{(k-1)k}} \quad (8)$$

defining the right-hand members as

$$\alpha_{(k-1)k} = \frac{y_{(k-1)}x_k}{y_k x_{(k-1)}} \quad (9)$$

In a binary mixture following Raoult's law,  $\alpha$  is constant at constant temperature, whence there can be no constant-evaporating mixture unless  $\alpha = D_2/D_1$ , in which case all mixtures of these components are constant-evaporating. In other words, despite the fact that such mixtures of liquids differing in boiling point can never be constant-boiling, they can be constant-evaporating. If two components of a complex mixture follow Raoult's law, the preceding statement applies to separation of these two components, whatever the volatility characteristics of the other constituents. The predominant effect of temperature on relative separation is likewise usually limited to its influence on  $\alpha$ , but its effect on rate of vaporization into a gas is great because of its effect on absolute volatility.



For the system methanol-benzene, the value of the ratio of the diffusion constants to be anticipated from the literature (4) is about 1.67; hence by Equation 7,  $\alpha$  for the constant-evaporating mixture is 0.6, corresponding to a concentration of 66 mole per cent methanol at 25° C. ( $\beta$ ). The constant-evaporating composition determined experimentally in the first part of this paper was 64 mole per cent methanol. (Because the calculation made no allowance for the mutual effect of the diffusion of the two vapors, each on the diffusivity of the other, the actual methanol content should be somewhat below the calculated.)

Equation 5 enables the change in concentration to be calculated as a function of the amount of evaporation. Substituting  $n_1/n_2 = u$ , separating variables, and integrating,

$$\int_{u_0}^u \frac{du}{(\alpha D_1/D_2 - 1)u} = \int_{(n_2)_0}^{n_2} \frac{dn_2}{n_2} = \ln \frac{n_2}{(n_2)_0} \quad (10)$$

where  $u_0$  and  $(n_2)_0$  refer to the value of these quantities at the beginning of the evaporation. Since  $\alpha$  is not a simple function of  $u$ , the definite integral on the left of Equation 10 is best evaluated graphically; the area under the curve obtained by plotting  $\frac{1}{(\alpha D_1/D_2 - 1)u}$  against  $u$  is equal to  $\ln n_2/(n_2)_0$ .

The weight per cent of the liquid evaporated,  $E$ , is obviously equal to

$$E = 100 \left[ 1 - \frac{n_2(m_2 + m_1u)}{(n_2)_0(m_2 + m_1u_0)} \right] \quad (11)$$

where  $m_1$  and  $m_2$  are the molecular weights of components 1 and 2.

### Results for Methanol-Benzene

Table C gives the results of such a calculation for the mixture containing initially 56 mole per cent methanol in benzene at 25° C., using the relative volatility data reported in a previous paper ( $\beta$ ). Figure 6 shows the agreement obtained with the experimental data on this mixture; the solid line is the calculated curve using a value of  $D_1/D_2 = 1.47$ , and the experimental points are indicated by the small circles. This value of relative diffusivity, 1.47, which must be employed accurately to fit these data, is equivalent to a constant-evaporating mixture of 62.4 per cent methanol, compared with the value of 64 per cent determined experimentally. The  $\ln n_2/(n_2)_0$  vs.  $u$  curve which results from the integration indicated by Equation 10 is very sensitive to small changes in  $u$  when this variable is near the constant-evaporating composition, since the left-hand member of Equation 10 becomes infinite at this point. Hence the calculation will be highly inaccurate unless the ratio of the diffusion constants and the variation of  $\alpha$  with composition are known precisely; in general, the farther it is from the constant-evaporating composition, the better the agreement.

It is obvious that the Rayleigh equation,

$$\frac{d \ln n_1}{d \ln n_2} = \alpha \quad (12)$$

can be integrated by a similar technic,

$$\int_{u_0}^u \frac{du}{u(\alpha - 1)} = \ln \frac{n_2}{(n_2)_0} \quad (13)$$

Figure 6 also shows in the curve marked Equation 13 the change in concentration, thus calculated, of the same initial mixture theoretically to be anticipated on simple distillation and hence also on true equilibrium evaporation. The Rayleigh equation, as already pointed out, differs from that for diffusional evaporation only in the omission of the relative diffusivity,  $D_1/D_2$ . Figure 6 also shows the experimental points obtained for this mixture in the Kunz bulb.

TABLE C. RESULTS OF CALCULATION FOR METHANOL-BENZENE MIXTURES

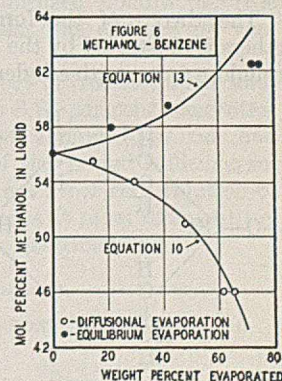
		(Assuming $D_1/D_2 = 1.47$ )						
Mole % Methanol	$u$	$\alpha$	$\ln \frac{(n_2)_0}{n_2}$	$\frac{(n_2)_0}{n_2}$	$\frac{m_2 + m_1u}{m_2 + m_1u_0}$	$1 - \frac{E}{100}$	$E$	
20	0.250	4.00	3.056	4.80	0.725	0.151	84.9	
30	0.429	2.46	2.898	4.10	0.772	0.188	81.2	
40	0.667	1.58	2.684	3.24	0.837	0.258	74.2	
50	1.000	1.04	2.174	1.985	0.935	0.471	52.9	
55	1.222	0.862	1.658	1.184	0.987	0.832	16.8	
56	1.272	0.830	1.489	1.00	1.00	1.00	0.0	

This calculated curve assumes complete homogeneity of the liquid and complete equilibrium of the final air-vapor mixture with it, conditions which the Kunz bulb does not achieve but only approximates. (The difficulties of securing complete equilibrium between a liquid mixture of volatile components and a gas bubbling through it have long been recognized, 9, 11.) Most of the evaporation in the bulb occurs near the bottom, setting up a concentration gradient which results in a rectification of sorts. Also, because the bulb does not achieve saturation of the gas, there is a residual diffusional effect. For small fractions evaporated, the first factor is apparently predominant in the set-up employed; for large percentage evaporation, the second overbalances the first, as is apparent from Figure 6. It did not seem necessary to try to achieve experimentally a closer approximation to true equilibrium evaporation into a gas, since this has been done by others (9) and the applicability of the Rayleigh equation to the equivalent vaporization of volatile mixtures by ebullition is unquestioned.

In short, while the change in concentration of mixtures of volatile solvents on evaporation into air under diffusional conditions differs widely from the corresponding change on ebullition (or equilibrium evaporation into air), the former change follows quantitatively the universally recognized Rayleigh equation for the latter, provided it is modified by introducing into it the relative diffusivities of the vapor components, as required by analysis of the mechanism of evaporation. The evaporative characteristics of volatile liquid mixtures can be predicted quantitatively from their physical properties, but in doing so diffusivities cannot be ignored when evaporating under conditions where diffusion plays a significant role.

It should be emphasized that all these equations assume the special conditions of diffusional evaporation already described. They must not be employed under ordinary practical conditions of evaporation from lacquer films, where usually the general movement of the air makes so-called eddy diffusion come into play (3), giving a result intermediate between what has here been called diffusional and equilibrium evaporation. An investigation of this case was made by Skljarenko and Baranajew (8), who found experimentally that under such conditions the ratio of the diffusivities in Equations 3, 5, and 7 should be raised, not to the first, but to the 0.5 power. Work of other investigators would indicate that the exponent should be somewhat higher (2, 5, 9). Obviously, in case of turbulent flow of the air, Equations 8 and 10 should be correspondingly modified.

Unlike the simple distillation of liquid mixtures under conditions of ebullition under their own vapor pressure, the evaporation of lacquer solvents is extraordinarily complicated.



Thus, the nonvolatile constituents of the lacquer influence the significant properties of the solvent mixture, both as to volatility and to diffusivity of the solvent constituents through the condensed phase. Furthermore, the noncondensable gases present undoubtedly affect both the relative and absolute volatilities of the solvents. Co-diffusion of the solvent vapors through the gas film modifies the diffusivity of each of the components.

As already pointed out, the conditions of flow of the gas past the surface of evaporation influence both turbulence and vapor concentration, and consequently modify the evaporative results (5, 7). Temperature effects due to heat absorption on evaporation must not be forgotten. The presence of condensable constituents—e. g., water vapor in the air—may easily be disturbing factors of major significance. All of these have been ignored in the preceding discussion because they are not relevant to the point at issue and many of them are usually of negligible significance in practical results.

However, the ultimate problem of solvent evaporation from lacquers will never be properly solved until all these factors have been adequately analyzed and their influence allowed for.

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RECEIVED August 11, 1936.

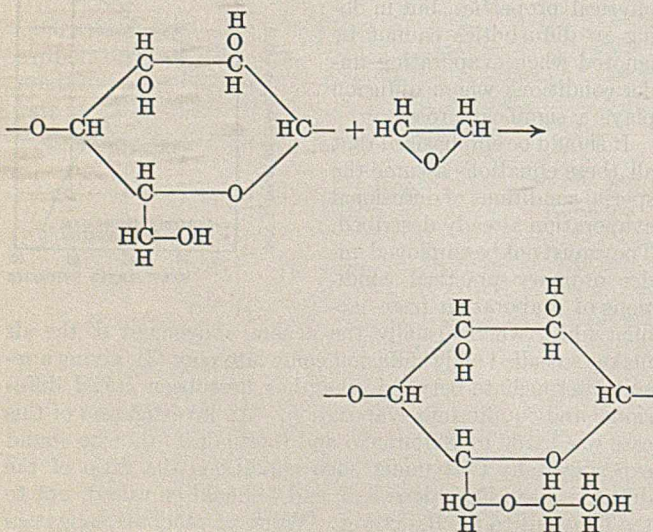
# Hydroxyalkyl Ethers of Cellulose

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**A**LKYL cellulose ethers were suggested as early as 1905 (6) and were later the subject of patents (2). The first reference to hydroxy ethers made from ethylene oxide was in 1923 (3); modified cellulose was used at elevated temperatures in the presence of a catalyst. At that time Dreyfus (1) patented the use of halogen derivatives of polyhydric alcohols.

The theory of the formation of hydroxyalkyl cellulose ethers is illustrated by the following typical reaction in which cellulose unites with ethylene oxide:



Starting with the work of previous investigators, the production variables were studied, improved manufacturing technic was devised, and finally a number of promising commercial applications were developed. The etherification reaction could be carried on to a desired extent simply by

controlling the proportions of cellulose to etherifying agent. The three hydroxyl groups in the cellulose molecule theoretically can react with alkylene oxides and chlorohydrins. Almost any degree of etherification is possible since the terminal primary hydroxyl of the attached alkyloxy groups may also react.

### Experiments with Ethylene Oxide

When working with ethylene oxide, alkali solubility of the resulting ethers increased as more ethylene oxide was used. Excellent solubility resulted when 13 per cent or more ethylene oxide was used (on the basis of the dry cellulose). Water solubility started at about 75 to 85 per cent.

Sodium hydroxide was found to be a useful agent in promoting etherification. One hundred grams of air-dry (5 per cent moisture) cotton linters were steeped in sodium hydroxide solution for 5 minutes at 25° C., drained, and again steeped. The following table shows some results obtained with various weights of this alkali cellulose and different degrees of etherification:

Soln. No.	NaOH in Mercerizing Caustic %	Weight of Alkali Cellulose Grams	Ethylene Oxide % of cellulose	Appearance of 1% Ether-6% NaOH Soln.
1	13	342	39	Almost insol.
2	18	314	38	Little better than 1
3	20	271	16	A few fibers not dissolved
4	25	310	25	Fairly good soln.
5	30	305	47	Almost perfect soln.
6	40	326	38	Almost perfect soln.
7	50	242	37	Almost insol.

An alkali cellulose was made from cotton linters steeped in 30 per cent sodium hydroxide at 25° C. for 5 minutes and centrifuged to a weight of three and one-third times the weight of the dry linters. The resulting alkali cellulose contained 29.3 per cent cellulose and 26 per cent sodium hydroxide. The following table shows results of etherifying this alkali cellulose with various amounts of ethylene oxide.

Soln. No.	% Ethylene Oxide	Appearance of 7% Ether-8% NaOH Soln.
1	12.0	Many undissolved fibers
2	14.7	Better than 1
3	16.65	Better than 2
4	17.2	Better than 3
5	18.5	Few undissolved fibrous residues
6	21.0	Almost perfect soln.
7	23.0	Almost perfect soln.
8	47.0	Almost perfect soln.
9	62.5	Almost perfect soln.
10	123.0	Almost perfect soln.

The ethers precipitated when the alkali was neutralized, with the exception of solution 10. This fact was utilized to coagulate the solution on glass plates to form films by immersing the coated glass in dilute sulfuric acid.

Because of their low strength it was impractical to produce films from solutions 8, 9, and 10; in fact, solution 10 was water soluble.

### Effect of Freezing

Since cellulose may be dispersed in alkali solutions by freezing, the possibility of using this method for improving the solubility characteristics of hydroxyethyl cellulose ether in alkali solutions was studied.

Using alpha-cellulose wood pulp<sup>1</sup> steeped in 30 per cent sodium hydroxide, aged 24 hours at 21° C., and etherified as shown in Table I, 8 per cent cellulose ether solutions were made up in a series of sodium hydroxide concentrations. These solutions were then frozen. The object was to determine the concentration of sodium hydroxide giving the best solution. After freezing and thawing, the sodium hydroxide was adjusted to 6.5 per cent in each case and the cellulose ether to 7.9 per cent.

TABLE I. EFFECT OF SODIUM HYDROXIDE CONCENTRATION DURING FREEZING

% NaOH in Ether Soln. <sup>a</sup> during Freezing	Relative Clearness <sup>b</sup> of Film	Filtration	Ethylene Oxide <sup>c</sup> %
No freezing	9	Almost impossible	13.25
2	5	Almost impossible	13.25
3	1	Almost impossible	13.25
4	1	Almost impossible	13.25
5	1	Easy	13.25
6	1	Easy	13.25
7	1	Difficult	13.25
8	1	Very difficult	13.25
10	5.25	Impractical	13.25
15	9	Impractical	13.25
20	10	Impractical	13.25
No freezing	1	Impractical	18
No freezing	1	Difficult	20

<sup>a</sup> Based on water plus sodium hydroxide.

<sup>b</sup> No. 1 was the clearest.

<sup>c</sup> Based on dry cellulose.

Table I indicates that no freezing yielded a very cloudy film. Freezing in 2 per cent sodium hydroxide represented an improvement, but the optimum concentration for clear films and easy filtration was found to be 5 to 6 per cent. Without freezing, filtration is impractical even though the ethylene oxide is raised to 18 per cent. Ethers with 20 per cent ethylene oxide filter difficultly in the absence of freezing.

When solutions of less than 20 per cent sodium hydroxide are frozen, water separates in the form of ice crystals (4). Probably the growth of ice crystals within the fibers disrupts the cellulose ether aggregates and, in the presence of sodium hydroxide, peptizes the ether. Under the microscope during thawing, the fibrillae of the cellulose fibers can be seen unwinding and dispersing.

### Experiments with Ethylene Chlorohydrin

Although ethylene oxide is the preferred etherifying agent, a study of the use of the chlorohydrin was made. The problems are similar to those encountered with ethylene oxide.

<sup>1</sup> Ninety-four per cent alpha-cellulose bleached sulfite wood pulp furnished by the Brown Company

Alpha-cellulose wood pulp was used as a source of cellulose. The alkali cellulose was shredded and aged overnight in the refrigerator at 5° C. Both the dry ethylene chlorohydrin<sup>2</sup> and aqueous solutions of it were used. A diluent was usually employed to promote uniform etherification. The aqueous solutions of the ethylene chlorohydrin were not miscible with either of the diluents—ethylene dichloride or benzene. After etherification the diluent was drained off, and the alkali ether spread out for a few minutes until the last traces of diluent were evaporated. The ethers were frozen with an 8 per cent cellulose concentration in 4.75 per cent sodium hydroxide solution in accordance with the best practice developed in working with the ethylene oxide derivative. The solutions prepared by freezing showed great improvement over those not frozen. The final solutions were adjusted to 7 per cent sodium hydroxide and 7 per cent cellulose for comparison.

The results indicate that the optimum concentration of mercerizing sodium hydroxide is approximately 43 per cent. The use of 40 per cent ethylene chlorohydrin, which is available commercially, gives results at least as good as those obtained with the dry chlorohydrin and ethylene dichloride diluent. Granulated pumice proved to be a satisfactory carrying agent for ethylene chlorohydrin and gave good results when used to carry the etherification agent for tumbling with the alkali cellulose. It was later filtered from the solution. The minimum ethylene chlorohydrin consistent with good solubility was 24.8 per cent of the dry cellulose. This corresponds to 13.5 per cent ethylene oxide, or approximately one glycol group to two C<sub>6</sub>H<sub>10</sub>O<sub>5</sub> units.

### Hydroxyethyl Cellulose Ethers

In this work 100 grams of air-dry (8 per cent moisture) wood pulp were used for each solution. In the preparation of the cellulose ethers, alkali cellulose was prepared from alpha-cellulose wood pulp steeped in 30 per cent caustic soda solution for 30 minutes at 20° C. Table II gives the results.

After etherification the alkali was neutralized with dilute sulfuric acid and the reaction product was thoroughly washed. The solubilities of the hydroxyethyl ethers (Table III) were determined under carefully standardized conditions; the separation of solubles from insolubles was effected by centrifugal means.

For the determination of the effect of freezing upon solubility, the ethers were made up to 8.75 per cent concentration with a solution of 4.75 per cent sodium hydroxide and frozen for 24 hours. At the end of this period sufficient sodium hydroxide was added to make a 2 per cent solution of the ether. After standing for 24 hours at room temperature, each was centrifuged and treated as described.

TABLE II. PREPARATION OF HYDROXYETHYL CELLULOSE ETHERS

Soln. No.	Aging of Alkali Cellulose at 21° C. <sup>a</sup>		Ethylene Oxide % of cellulose	Soln. No.	Aging of Alkali Cellulose at 21° C. <sup>a</sup>	
	Hours	Grams			Hours	Grams
1	16.75	2.2	4	5	19.75	7.65
2	17.5	3.28	6	6	22.25	9.83
3	18.5	4.37	8	7	23.25	13.10
4	19.0	5.46	10	8	24.25	16.38

<sup>a</sup> 200 grams used in each case with 27.3% cellulose.

The dihydroxypropyl cellulose ether was prepared from glycerol alpha-monochlorohydrin by reactions with alkali cellulose. In preparing this compound, the use of 25 per cent sodium hydroxide for steeping proved to be about the optimum.

<sup>2</sup> From Eastman Kodak Company, specific gravity 1.192 at 24° C.

TABLE III. PER CENT SOLUBILITY OF DRY HYDROXYETHYL CELLULOSE ETHERS IN SODIUM AND POTASSIUM HYDROXIDES

Ethylene Oxide <sup>a</sup>	% NaOH					% KOH						
	2.05	5.0	15.0	19.8	25.08	29.95	5.0	10.0	15.0	20.0	25.0	30.0
	Not Frozen											
4	7.0	16.5	27.6	14.7	9.0	4.0	..	..	..	..	6.7	7.5
6	6.8	14.3	..	10.7	10.5	5.9	..	..	..	..	6.0	6.5
8	3.5	33.0	..	7.0	13.0	9.5	..	..	..	15.0	15.9	11.0
10	6.5	58.3	..	19.0	..	..	..	..	..	..	..	..
14	4.5	68.6	..	..	..	..	..	5.7	7.3	..	..	..
18	15.0	85.1	54.2	..	1.3	2.5	..	11.3	12.5	..	..	..
24	25.7	..	..	..	7.3	2.5	14.2	20.0	..	..	..	..
30	43.3	..	81.7	2.9	..	..	8.7	28.3	..	..	..	..
	Frozen											
4	50.5	64.2	39.2	30.4	..	..	..	..	..	..	1.9	2.4
6	38.8	69.6	..	17.5	2.6	2.2	..	..	..	..	1.2	1.4
8	82.1	80.0	..	22.4	8.0	2.5	..	..	..	..	1.5	0.4
10	78.3	92.0	..	33.3	6.4	2.3	..	..	..	21.4	..	..
14	95.3	97.07	..	..	1.4	2.3	..	21.6	16.7	..	..	..
18	95.7	99.2	..	..	14.8	4.0	..	42.6	19.6	..	..	..
24	97.6	99.7	..	..	13.7	11.6	21.5	30.7	..	..	..	..
30	95.1	100.0	98.2	34.3	..	..	18.2	58.0	..	..	..	..

<sup>a</sup> In per cent of dry cellulose.

The hydroxyethyl cellulose ether can be precipitated from alkali solution by neutralizing the alkali. This property was utilized for permanently sizing cloth, such as damask, by treating the cloth with the ether solution, coagulating in acid solution, washing, and drying. The cloth could also be treated with alkali and ethylene oxide to etherify the surface superficially, followed by coagulation.

### Semi-commercial Production

At the time that films were made on a semi-commercial scale, the production of the ether solution was standardized as follows: Alpha-cellulose pulp was cut into sheets, 5.75 × 4.25 inches, and steeped in small charges (4.45 pounds, dry basis) of pulp in about eighteen times its weight of 30 per cent sodium hydroxide solution at 17° C. for 45 minutes. The alkali cellulose was then pressed to 14.5 to 15.0 pounds, and shredded for 1.5 hours in a Baker-Perkins shredder cooled with jacket water to maintain a temperature of 18° to 19° C. in the alkali cellulose. The alkali cellulose was aged in loosely covered cans for 18 to 21 hours at 17° C. The etherification was performed in a churn which was evacuated before introducing 0.52 pound of ethylene oxide. Four hours later the charge was dumped, and 3.15 pounds of the alkali ether were neutralized and added to the rest in a mixer with water to make 63 pounds of solution. This was frozen at -26° C. for 48 hours and then mixed with sodium hydroxide solution to make 70 pounds of solution. The solution was filtered and the air removed with a vacuum.

The solution was extruded by air pressure, through an illium alloy head into a bath of 15 to 20 per cent sulfuric acid, with sufficient sodium sulfate to maintain the specific gravity at 1.20 to 1.28 (corresponding to 11-15 per cent sodium sulfate). This treatment coagulated the sheet which was then washed in running water in a series of tanks. The film was extruded at a rate of 10 feet per minute. It was found that, unless some emollient was introduced, the dry film was brittle. Therefore, the sheet was run through a bath of 2 per cent glycerol prior to reeling.

Although the sheet was extruded from a slot 16 inches long, it shrank to about 12.5 inches during coagulation and in traversing the machine. The rates of extrusion and reeling were balanced to maintain a thickness of 0.008 inch.

If the sheet narrowed too much, it was usually found that the acid was too weak or too cold. Scraps of film could be dissolved and used again by freezing in an alkaline solution. Unless freezing was resorted to, the dissolving action was very slow. This held true for both sodium and potassium hydroxide solutions. For example, the wet film when frozen in 4.75 per cent sodium hydroxide solution readily dissolved.

The wet film could be cut in strips and used to seal bottles. Upon drying, the strip shrank and adhered to itself when wrapped in overlapping relation.

The wet film contained 88 per cent water. If dried loosely, it shrank out of shape. Therefore, it was dried on a drum-type paper dryer.

Since it is usually cheaper to freeze water than to evaporate it, freezing of the film was tried with the object of eliminating water. It was found that 55 to 60 per cent of the water in the freshly formed film could be eliminated. At the same time the shrinkage, compared to that when dried freely, was reduced from about 35 to 8 per cent. This makes it possible for a commercial plant to eliminate much of the conventional drying equipment and at the same time to reduce operating costs.

Another advantage resulting from freezing is that the film has a more uniform strength along and across the sheet. Using a sheet of hydrated cellulose freshly precipitated from viscose, it was found that the moisture loss due to freezing was 57 per cent.

Care must be exercised in freezing films because, if it takes place too quickly, the films become permanently opalescent. This behavior is probably due to distortion by ice crystals. The minimum temperature consistent with clear films in stagnant air under the conditions of the work was found to be 8° F. It proved feasible to freeze the film in cold brine, the freezing taking place before the salt diffused into the film.

In commercial use, transparent sheets are subject to wide humidity changes, and it is desirable that the area should not change. A study of the hydroxy ether films indicated considerably less change in area than occurred in commercial viscose sheets.

Films made and dried on the drum dryer were humidified at 65 per cent relative humidity and tested for breaking strength and ultimate elongation on a standard Schopper paper testing machine. The following are typical tests for films 0.00095 inch thick:

Material	Viscosity Sec.	Glycerol <sup>a</sup> %	Ultimate strength Kg.	Direction Ultimate elongation %	Across the Sheet	
					Ultimate strength Kg.	Ultimate elongation %
Hydroxy ether film	14	4	1.96	12.1	1.68	20.3
	68	4	3.75	20.45	2.61	31.6
	68	2	3.90	8.6	3.38	24.0
	68	0	5.22	8.6	4.58	13.0
	68	1	4.43	11.6	..	..
Commercial viscose sheets <sup>b</sup>			2.20	3.24	1.6	12.31
			3.70	12.6	2.12	23.4
			2.95	8.24	1.89	37.7

<sup>a</sup> In bath.

<sup>b</sup> Regenerated cellulose.

The ether film made under proper conditions greatly surpassed the commercial viscose film in strength without sacrificing elongation. The elongation across the sheet is always greater than in the machine direction. The ether film was more nearly uniform in this respect than commercial viscose film.

### Commercial Possibilities

Encouraged by the many advantages of the hydroxyethyl cellulose ether films over commercial regenerated cellulose made from viscose, an analysis was made which indicated that the cost of producing the ether film would compare favorably with the cost of film made by the viscose method. Ease of control, simplicity of production, and the possible re-use of scraps also favor the use of the cellulose ether.

Rayon was spun from the ether solution on a Topham

bucket-type spinning machine. The rayon resembled viscose rayon. Although the dry strength was excellent, the wet strength was low. By forming a urea-formaldehyde resin in the rayon, it was possible to obtain a wet strength substantially equal to the dry strength.

In addition to developing a number of commercial possibilities in which the hydroxyethyl ether is used directly, some of its derivatives were prepared. It could be nitrated readily to yield an excellent lacquer base with low viscosity and excellent clarity and stability.

When cellulose is acetylated, it is usually necessary to go through a second hydrolytic step to achieve acetone solubility. In contrast, the hydroxyethyl dicellulose ether may be acetylated to yield in one step almost perfect acetone solubility. Films of the acetyl derivatives show good physical properties. As the degree of alkylation increases, the ether may be acetylated more easily.

The stearate, xanthate, and benzoyl derivatives were made. These and the methylated ether were similar to the corresponding cellulose derivatives. Doubtless, many other derivatives can be prepared.

The data presented represent a brief summary of the re-

search work of several years. Further details are given in patents (5).

### Acknowledgment

The authors wish to thank the C. F. Burgess Laboratories, Inc., and the Carbide and Carbon Chemicals Corporation for their courtesy in permitting the publication of this paper.

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RECEIVED May 6, 1936.

# Refractive Index of Egg Albumen

## Changes with Age, Season, and Development

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**P**ROTEIN solutions, because of their chemical complexity and amphoteric nature, are usually difficult to characterize by ordinary chemical methods. Physical measurements, on the other hand, are particularly applicable because of the large molecular weights involved.

It has often been shown that the refractive index of a protein solution is an indication of the amount of protein present. From the electromagnetic theory of light it is evident that the refractive power of protein solution must be due to the volume occupied by the protein molecules. Consequently, such factors as temperature, bound water, and degree of dispersion of the protein will influence the refractive index of its solution (6).

In dealing with the albumen of birds' eggs, the problem is more complicated, not only because of the presence of several proteins, but also because four natural divisions or layers of albumen are clearly distinguishable in the fresh egg. These layers are differentiated morphologically during the process of egg formation. Each layer, presumably, is destined to carry on distinct biological functions at least in the early course of embryonic development. Therefore, it may logically be assumed that each layer is of different chemical structure and consequently of different refractive properties.

As a part of the investigation of various physico-chemical properties of albumen of birds' eggs, an extensive study of the refractive index was made. The object was to establish (1) the exact values of four layers of albumen of the fresh eggs of several representative species of birds, (2) the frequency distribution in a flock of hens, (3) the variation within a normal breeding and incubating season, (4) the constancy with individual birds, (5) the changes in the unfertilized

eggs with age under low and high temperatures, and (6) the changes in the fertilized incubated eggs.

### Materials and Methods

A large number (1177) of eggs of the following species was used: white Leghorn chickens (*Gallus domesticus*), ring-necked pheasants (*Phasianus torquatus*), bobwhite quail (*Colinus virginianus*), Bourbon red turkeys (*Meleagris gallopavo*), and white Peking and white runner ducks (*Anas domesticus*).

Usually all the eggs were tested within 12 hours after being laid. Prior to the analysis they were kept in the refrigerator at about 40° C. and 70 per cent relative humidity. In special tests of strictly fresh eggs, the eggs were used not later than half an hour after they were laid.

The various layers of egg albumen were separated and sampled. The egg was broken into two parts, and the contents dropped gently into a large Petri dish. Then the layers were removed by means of pipets in the following order: (1) the outermost fluid layer with a pipet having a bore at the point 1 mm.; (2) the middle fluid layer with the same pipet, after making an incision in the sac of the dense albumen with scissors and permitting the fluid of this layer to run out; (3) the middle dense layer with a pipet having a bore at the point 2 mm.; and (4) the innermost chalaziferous layer together with the chalazas was removed with forceps.

The refractive index was read at 25° C. with a Zeiss refractometer, Abbe type.

### Strata of Fresh Egg Albumen

Table I shows that there is a noticeable difference in the refractive index of the different layers of albumen of the eggs just laid.<sup>1</sup> The value was lowest for the outer fluid

<sup>1</sup> The proportional amounts by weight of each layer of chicken egg albumen, for example, was found to be 23.18, 57.29, 16.84, and 2.69 per cent of outer fluid, middle dense, middle fluid, and chalaziferous layer, including the chalazas, respectively.

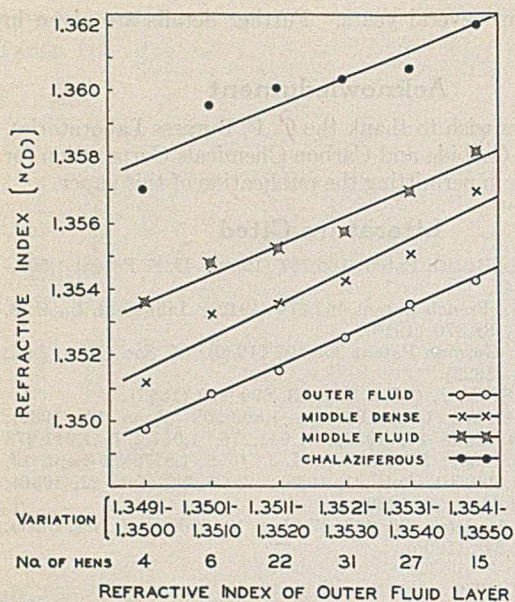


FIGURE 1. FLOCK DISTRIBUTION OF 105 HENS, BASED ON REFRACTIVE INDEX OF OUTER FLUID LAYER OF ALBUMEN

layer; it increased with each consecutive layer inward, irrespective of their apparent densities. The general relation for the refractive index of the various layers of albumen is the same for the eggs of all species studied.

However, the separation of albumen by means of a screen into only two layers—the dense (or firm) and the liquid layer (when the latter includes both the outer fluid and the middle fluid portions)—as has been done by some workers (1, 4), did not reveal any difference in the refractive index between these two samples. To explain such a phenomenon, the data on more than 500 fresh chicken eggs (not over 12 hours old) were compiled, using for comparison the refractive index of the dense portion and of the fluid portion of albumen (outer fluid and middle fluid combined); on the average, the refractive index of both samples came to the same value of 1.3540.

### Frequency Distribution in the Flock of Hens

To find the variability in the average refractive indices of the four layers of egg albumen of individual birds, 105 white Leghorn hens from two to three years old were used. Up to eight eggs from each hen were examined.

Figure 1 illustrates the flock distribution based on the refractive index of the outer layer of albumen. In each of the six groups of hens the average value for the refractive index of the outer layer is arranged within the limits of

TABLE I. REFRACTIVE INDEX OF VARIOUS LAYERS OF FRESH EGG ALBUMEN

Species	No. of Eggs	Refractive Index, $n_D$			
		Outer fluid	Middle dense	Middle fluid	Chalaziferous
Chicken	717	1.3529	1.3552	1.3582	1.3606
Pheasant	6	1.3560	1.3567	1.3575	1.3588
Quail	5	1.3568	1.3581	1.3590	1.3603
Turkey	5	1.3535	1.3561	1.3594	1.3628
Duck:					
Peking	4	1.3542	1.3557	1.3569	1.3612
Runner	5	1.3565	1.3580	1.3598	1.3630
Average	...	1.3550	1.3566	1.3585	1.3611

0.0001 to 0.0010. The curves for the different layers are nearly parallel. Therefore the same relation seems to exist between the different layers, regardless of their absolute values.

Biologically the refractive index may be of some significance in the reproduction of birds. Among 775 incubated eggs, 29.1 per cent was infertile from hens laying eggs with a high refractive index of albumen and 41.1 per cent was infertile from hens laying eggs with a low refractive index. The difference,  $12.0 \pm 3.40$ , is statistically significant. On the other hand, the hatchability of fertile eggs was almost the same in both groups of hens.

### Variation within the Breeding Season

For the period of 7 months from December to June, inclusive, there were used for the study of the refractive index of various layers of albumen, fifty chicken eggs on an average every month from the same group of hens. The observations

(Figure 2) indicate that the refractive index of albumen is highest just at the beginning of the natural breeding season—that is, from February to March. The values of all four layers of albumen are lowest at the closing of the breeding season in July.

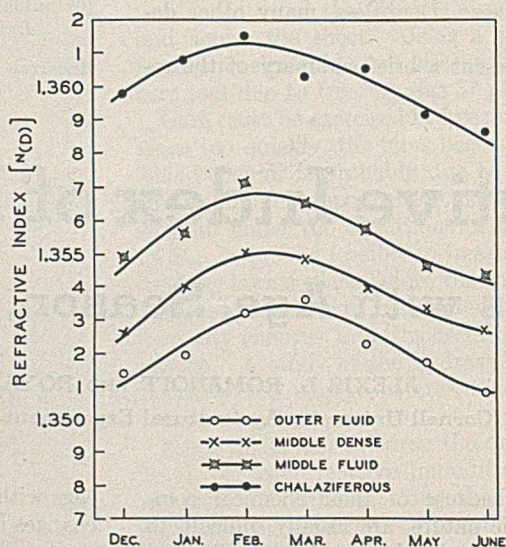


FIGURE 2. SEASONAL CHANGES IN REFRACTIVE INDEX OF LAYERS OF EGG ALBUMEN FROM A GROUP OF TWELVE HENS

### Constancy with Individual Hens

Observations showed that the refractive index of egg albumen is a constant characteristic of an individual hen.

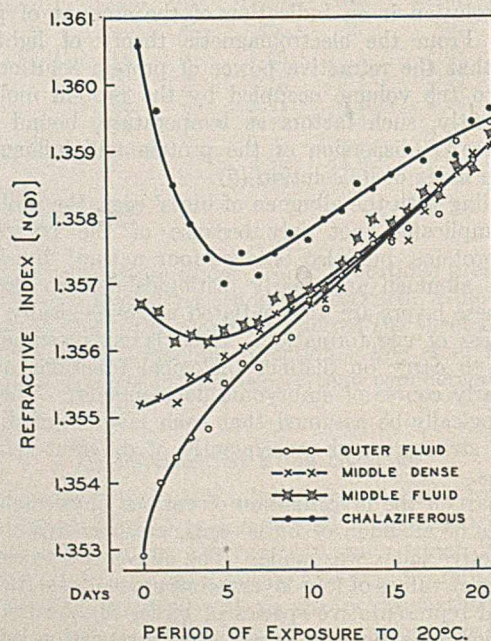


FIGURE 3. CHANGES WITH AGE IN REFRACTIVE INDEX OF LAYERS OF FRESH EGG ALBUMEN FROM SEVEN HENS

The hen, which lays eggs with either a high or low refractive index of albumen, maintains that value throughout the breeding season. Furthermore, the seasonal changes were found to be much more pronounced with the birds possessing low refractive indices than in those with high indices (Table II).

TABLE II. SEASONAL CHANGES IN REFRACTIVE INDEX OF VARIOUS LAYERS OF ALBUMEN OF FRESH CHICKEN EGGS FROM TWO GROUPS OF BIRDS\* EXHIBITING HIGH AND LOW INDICES

Season	Outer Fluid		Middle Dense		Middle Fluid		Chalaziferous	
	High	Low	High	Low	High	Low	High	Low
December	1.3530	1.3497	1.3553	1.3498	1.3577	1.3523	1.3642	1.3555
January	1.3532	1.3513	1.3554	1.3532	1.3570	1.3549	1.3618	1.3603
February	1.3541	1.3517	1.3556	1.3539	1.3581	1.3553	1.3619	1.3609
March	1.3542	1.3526	1.3550	1.3544	1.3569	1.3558	1.3613	1.3687
April	1.3533	1.3510	1.3549	1.3528	1.3568	1.3545	1.3619	1.3590
May	1.3527	1.3508	1.3542	1.3524	1.3551	1.3542	1.3604	1.3578
June	1.3512	1.3503	1.3539	1.3515	1.3554	1.3531	1.3588	1.3584

\* Six in each group.

b The figures are averages of about 25 eggs from each group of birds per month.

### Changes in Unfertilized Eggs with Age

The attempt was made to trace the precise changes in the refractive index of various layers of albumen of chicken eggs with age. The unfertilized eggs from the same group of hens were tested either immediately after laying or after storing at 20° C. and 60 per cent relative humidity for various periods up to 21 days. The results of observations (Figure 3) show that differences in the refractive properties of various strata of egg albumen rapidly diminish immediately after the egg is laid and, of the first three layers, almost completely disappear within 3 to 5 days.

Presumably because of this rapid change in the distinct refractive properties of various strata of egg albumen with age, the majority of workers failed to recognize such differences. In the use of eggs not strictly fresh, it appears possible to obtain the same values of the refractive index for all three layers, and to interpret the data of further changes as one linear curve of increase with age of the eggs (4).

The eggs of five species of birds when incubated at 37.5° C. and 60 per cent relative humidity also show a gradual, almost linear, increase in the refractive index of the outer fluid and of the middle dense layer of albumen. The refractive index of the inner chalaziferous portion of albumen, particularly of the chalazas, was little changed (Figure 4); a slight drop occurred at one week of age, corresponding to that observed at 20° C. The refractive index of the middle fluid layer soon approached the value of the middle dense layer, which at the

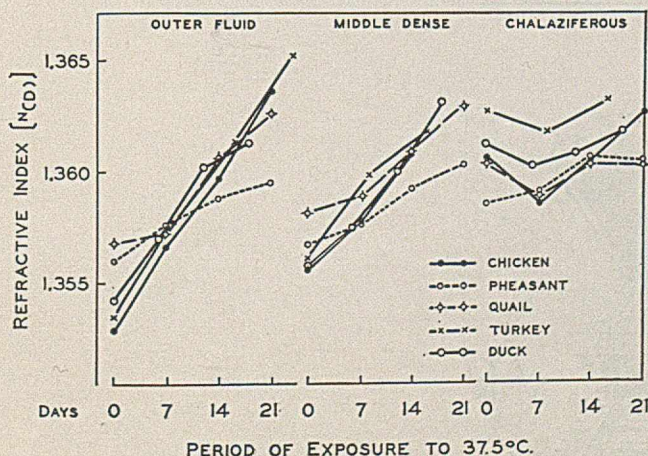


FIGURE 4. RELATIVE CHANGES IN REFRACTIVE INDEX OF ALBUMEN OF UNFERTILIZED INCUBATED EGGS. Each point represents from three to five observations.

age of about one week practically disappeared as a morphologically distinct layer.

### Changes in Fertilized Incubated Eggs

During incubation there is rapid disintegration in the strata of albumen of the developing egg. At the end of 24 hours the middle fluid layer almost completely disappears. After 3 to 4 days of incubation, the middle dense layer disappears. The inner chalaziferous layer also disappears in the early period of the development of the egg, except the chalazas which are found to be floating loosely in the structureless mass of albumen resembling the outer fluid layer.

This process of disintegration in the strata of albumen of fertilized incubated eggs is presumably due to a rapid dehydration, or loss of water, at the expense of external evaporation, on the one hand, and of transference of water to the yolk, on the other (10). Since the refractive index has a direct relation to the density or to the solid content of the colloidal solution, rapid change in the refractive index of the disintegrated egg albumen would be expected in the course of embryonic development.

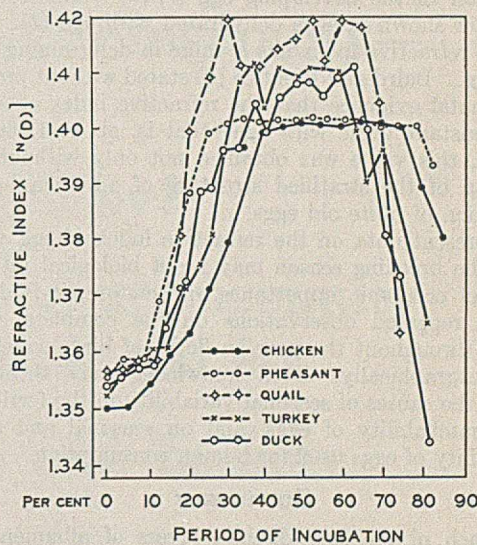


FIGURE 5. RELATIVE CHANGES IN REFRACTIVE INDEX OF ALBUMEN FROM DEVELOPING EGGS

Each point represents from four to six observations.

Observations on eggs of five species of birds show that the refractive index of the disintegrated or composite "outer" layer of albumen increased rapidly with the incubation period (Figure 5). It reached the maximum value during the first third of the period, then remained almost constant during the second third, and finally had a sudden drop to a low value. Although the curves of these changes in the eggs of various species of birds vary slightly, they could not be interpreted definitely in terms of the specificity of various albumens. All the curves follow one general trend as just described and shown in Figure 5. It is interesting to note that these changes coincide well with changes in the reciprocal of electrical conductivity (9).

### Discussion

Reiss (5) showed that the index of refraction of a protein solution is directly proportional to its concentration. Consequently, the four layers of fresh egg albumen are of different concentration, as has already been demonstrated experi-

mentally (8). The writers' recent observations indicate that the dry matter of the outer fluid, middle dense, middle fluid, and chalaziferous layers of albumen of fresh chicken eggs is, on an average, 10.70, 12.85, 13.72, and 15.82 per cent, respectively. Also the densities of these four representative layers of albumen are found to be 1.03149, 1.03457, 1.03690, and 1.04685. Thus the present data on the refractive indices of various strata of albumen agree very well with their dry matter and density—that is, with their concentration.

There is considerable difference, as may be expected, between the refractive index of albumen of a developing egg and that of an unfertilized egg hydrolyzed and partially decomposed with age. During the process of embryonic development, the egg albumen, besides being hydrolyzed through the loss of water externally and through the transference into the yolk and to the developing embryo, presumably undergoes certain chemical transformations caused by the preferential absorption of certain proteins and protein-fraction amino acids. The change in the chemical composition unquestionably would influence the refractive index of egg albumen (3).

However, the greatest change in the refractive index of albumen is due to changes in concentration. Consequently, there is a direct relation between the refractive index and the dry matter of the developing egg (7, 10). This relation is still better shown in eggs dehydrated with age (1). Therefore, the refractive index has a value in determining the age of the egg. Baird and Prentice (2) stated without presenting experimental evidence that the refractive index of albumen has a constant value with age—that is, about 1.360. Presumably, this value was obtained not only without a consideration of the stratified structure of albumen but from observation of quite old eggs.

The present data on the refractive index of egg albumen within the breeding season may be of biological interest as well as of economic importance. Therefore, it is desirable to have repeated observations on the complete cycle of changes throughout the year on flocks of birds widely separated geographically. Such knowledge may throw more light on the causes of seasonal variability in the fertility and in the hatchability of eggs, and on seasonal and regional perishability of eggs used for human consumption.

### Summary

1. Each of the four distinct layers of albumen in the fresh eggs of chicken, pheasant, quail, turkey, and duck

shows specific refractive properties. The actual values of the refractive index increase with the successive layers, from the outermost to the innermost layer; on an average for 717 chicken eggs the values are 1.3529, 1.3552, 1.3582, and 1.3606.

2. The refractive index of albumen of fresh eggs varies seasonally. Its value is highest at the beginning of the natural breeding and incubating season from February to March.

3. The refractive index of albumen as observed in 105 hens is characteristic of the individual birds. Throughout the breeding season the same relation exists between the different layers of albumen, regardless of the absolute value.

4. The refractive index of albumen of unfertilized eggs increases linearly with age because of dehydration in all layers except the innermost (chalaziferous) layer, in which it drops, then reaches its original value, and thereafter remains constant. This change in the refractive index with the constant humidity of 60 per cent is more rapid at a high (37.5°) than at a low temperature (20° C.).

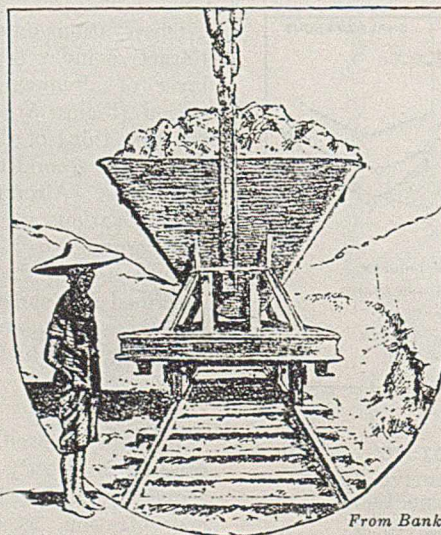
5. During the incubation of fertilized eggs, there is rapid disintegration in the strata of albumen. The refractive index of this disintegrated albumen increases rapidly with the incubation period. It reaches the maximum value of about 1.40–1.42 during the first third of the period, then remains almost constant during the second third, and finally has a sudden drop to a low value.

6. Since the refractive index of albumen of birds' eggs has a direct relation with the concentration and density, it is an approximate measure of the total solids of the various layers of albumen.

### Literature Cited

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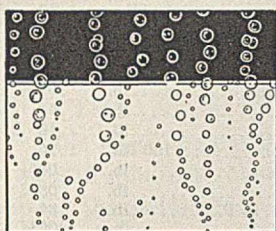
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## MARKET REPORT (continued from page 38)

<div style="font-size: small;"> <p>                     Dianisidine, bbls.....lb. 2.25                      Dibutoxyethyl phthalate, wks., drums                          .....lb. .42                      Dibutyl ether, drums, wks.....lb. .22                      Dibutylphthalate, drums, wks., frt.                          allowed.....lb. .18                      Dibutyl tartrate, drums.....lb. .35                      Dichlorethyl ether, drums, c/l, wks.....lb. .16                      Dichloropentanes, tanks, wks.....lb. .02½                      Diethanolamine, drums, wks.....lb. .31                      Diethylaniline, drums.....lb. .50                      Diethylene glycol, drums, wks.....lb. .16½                          Monobutyl ether, drums, wks.....lb. .26                          Monoethyl ether, drums, wks.....lb. .16                      Diethylene oxide, drums, wks.....lb. .20                      Diethyl carbinol, drums, wks.....lb. .60                      Diethyl phthalate, drums.....lb. .18½                      Diethyl sulfate, tech., drums, wks.....lb. .20                      Diglycol oleate, drums.....lb. .24                      Dimethylamine, pure 25.40% sol.—                          100% basis, drums.....lb. .95                      Dimethylaniline, drums.....lb. .28                      Dimethyl ethyl carbinol, drums, wks.....lb. .60                      Dimethylsulfate, drums.....lb. .45                      Dimethyl phthalate, drums, wks., frt.                          allowed.....lb. .19½                      Dinitrobenzene, tech., drums.....lb. .17                      Dinitrochlorobenzene, bbls.....lb. .14½                      Dinitronaphthalene, bbls.....lb. .35                      Dinitrophenol, bbls.....lb. .23                      Diphenyl.....lb. .15                      Diphenylamine, bbls.....lb. .31                      Diphenylguanidine, bbls.....lb. .35                      Epsom salt, tech., bbls., c/l, N. Y.                          100 lbs.....1.80                      Ether, conc., drums.....lb. .09                      Ether, nitrous, bot.....lb. .75                      Ethyl acetate, tanks, c/l, wks., frt.                          allowed.....lb. .06½                      Acetoacetate, 110-gal. drums, wks.,                          frt. allowed.....lb. .37                      Bromide, drums.....lb. .50                      Carbonate, 90%, 50-gal. drums.....gal. 1.85                      Chlorcarbonate, carboys.....lb. .30                      Chloride, drums.....lb. .22                      Ether, absolute, 50-gal. drums.....lb. .50                      Furoate, 1-lb. tins.....lb. 5.00                      Methyl ketone, drums.....lb. .07½                      Ethylbenzylaniline, 300-lb. drums.....lb. .86                      Ethylene dichloride, drums, wks.,                          frt. allowed.....lb. .05½                      Ethylenechlorohydrin, anhyd.,                          drums, wks.....lb. .75                      Glycol, c/l, wks.....lb. .17                      Monobutyl ether, drums, wks.....lb. .20                      Monoethyl ether, drums, wks.....lb. .16                      Monoethyl ether acetate, drums,                          wks.....lb. .14                      Monomethyl ether, drums, wks.....lb. .19                      Oxide, cylinders, wks.....lb. .60                      Feldspar, bulk.....ton 10.00                      Ferric chloride, tech., bbls.....lb. .05                      Ferrous sulfide, bbls.....100 lbs. 2.50                      Fluorspar, 98%, bags.....ton 31.00                      Formaldehyde, bbls.....lb. .05½                      Formalin, drums.....lb. .37½                      Fuller's earth, bags, c/l, mines.....ton 6.50                      Furfural, drums, tech., contract,                          works.....lb. .10                      Glauber's salt, bbls.....100 lbs. 1.05                      Glucose, 70°, bags, dry.....100 lbs. 3.28                      Glycerine, c. p., drums.....lb. .21½                      Glyceryl phthalate, drums.....lb. .30                      Glycol phthalate, drums.....lb. .29                      Stearate, drums.....lb. .23                      G salt, bbls.....lb. .45                      Hexamethylenetetramine, tech.,                          drums.....lb. .35                      Hydrogen peroxide, 25 vol., bbls.....lb. .05½                      Hydroquinone, kegs.....lb. 1.20                      Indigo, 20% paste, bbls.....lb. .12                      Iodine, resubl., jars.....lb. 1.50                      Iron acetate, liq., 17°, bbls., c/l.....lb. .03                      Isobutyl carbinol (128-132° C.),                          tanks.....lb. .32                      Kieselguhr, bags.....ton 50.00                      Lead, metal, N. Y.....100 lbs. 5.30                      Lead acetate, drs., white.....lb. .11                          Arsenate, drs.....lb. .09                          Oxide, litharge, bbls., 20-ton lots.....lb. .068                          Peroxide, drums.....lb. .46                          Red, bbls., 20-ton lots.....lb. .078                          Sulfate, bbls.....lb. .06½                          White, basic carb., bbls.....lb. .06¾                      Lime, hydrated, bbls.....100 lbs. 85                      Lime, live, chemical, bbls., wks.....                          280 lbs. 1.70                      Limestone, ground, bags, wks.....ton 4.50                 </p> </div>	<div style="font-size: small;"> <p>                     Lithopone, bbls.....lb. .04¼                      Magnesite, calcined, 500-lb. bbls.,                          wks.....ton 60.00                      Magnesium, metal, wks.....lb. .30                      Magnesium carbonate, bags.....lb. .06                      Chloride, drums.....ton 36.00                      Fluosilicate, cryst., bbls.....gal. .10                      Oxide, U. S. P., light, bbls.....lb. .42                      Manganese chloride, casks.....lb. .07½                      Dioxide, 85-90%, bbls.....ton 57.50                      Sulfate, casks.....lb. .07                      Manitol, pure, cryst., cs., wks.....lb. 1.48                      Mercury bichloride, cryst., 100 lbs.....lb. 1.40                      Mercury flasks, 76 lbs.....flask 93.00                      Meta-nitroaniline, bbls.....lb. .87                      Meta-phenylenediamine, bbls.....lb. .82                      Meta-tolylendiamine, bbls.....lb. .65                      Methanol, pure, synthetic, drums,                          wks., frt. allowed, c/l.....gal. .40                          Tanks, wks., frt. allowed.....gal. .35½                      Methyl acetone, tanks, wks., frt.                          allowed.....gal. .41                      Methyl chloride, cylinders.....lb. .37                      Hexyl ketone, drs., tech., wks.....lb. .60                      Methyl propyl carbinol, drums, wks.....lb. .60                      Methyl salicylate, cases.....lb. .42                      Michler's ketone, bbls.....lb. 2.50                      Monoamylamine, drums, wks.....lb. 1.00                      Monoethanolamine, drums, wks.....lb. .31                      Monomethylamine, drums.....lb. .75                      Naphthalene, flake, bbls.....lb. .07¼                      Nickel, metal.....lb. .35                      Nickel salt, single, bbls.....lb. .13                          Double, bbls.....lb. .13                      Niter cake, bulk.....ton 5.00                      Nitrobenzene, drums.....lb. .08                      Nitrogen solution unit.....unit 1.04                      Octyl acetate, tanks, wks.....lb. .15                      Oil, castor, No. 1.....lb. .10¾                          China wood, bbls.....lb. .13¾                          Coconut, tanks.....lb. .08                          Cod, N. F., bbls.....gal. .48½                          Corn, crude, tanks, mills.....lb. .09¾                          Cottonseed, oil refined, bbls.....lb. .10½                          Linseed, boiled, bbls.....lb. .097                          Menhaden, crude, tanks.....gal. .35                          Neat's-foot, pure, bbls.....lb. .11½                          Oleo, No. 1, bbls.....lb. .10¾                          Olive oil, denat., bbls.....gal. 1.45                          Foots, bbls.....lb. .09¼                      Peanut, crude, tanks.....lb. .09¾                      Perilla, bbls.....lb. .10½                      Rapeseed, bbls.....gal. .75                      Red, bbls.....lb. .10¾                      Soy bean, crude, tanks.....lb. .09½                      Spermaceti, 38°, bbls.....lb. .098                      Whale, bbls., natural, refined.....lb. .079                      Ortho-aminophenol, kegs.....lb. 2.15                      Ortho-dichlorobenzene, drums.....lb. .05                      Ortho-nitrochlorobenzene, drums.....lb. .28                      Ortho-nitrophenol, bbls.....lb. .85                      Ortho-nitrotoluene, drums.....lb. .07                      Ortho-toluidine, bbls.....lb. .14                      Paraldehyde, 110-50-gal. drums.....lb. .16                      Para-aminophenol, kegs.....lb. 1.05                      Para-dichlorobenzene.....lb. .16                      Para-formaldehyde, cases.....lb. .38                      Paraldehyde, tech., drums.....lb. .16                      Para-nitraniline, drums.....lb. .45                      Para-nitrochlorobenzene, drums.....lb. .23½                      Para-nitrophenol, bbls.....lb. .35                      Para-nitrosodimethylaniline, bbls.....lb. .92                      Para-nitrotoluene, bbls.....lb. .36                      Para-phenylenediamine, bbls.....lb. 1.25                      Para-tertiary amyl phenol, drums,                          c/l, wks.....lb. .26                      Para-toluidine, bbls.....lb. .56                      Paris Green, 250-lb. kegs.....lb. .23                      Perchlorethylene, drs., frt. allowed.....lb. .10½                      Phenol, drums.....lb. .13¼                      Phenolphthalein, yellow, drums.....lb. .70                      Phenylethyl alcohol, 1-lb. bot.....lb. 3.75                      Phloroglucinol, tech., drums.....lb. 15.00                          c. p., drums.....lb. 20.00                      Phosphorus, red, cases.....lb. .40                      Oxylchloride, 175-lb. cylinders.....lb. .16                      Trichloride, cyl.....lb. .16                      Phthalic anhydride, bbls.....lb. .14½                      Platinum, metal, solid.....oz. 45.00                      Potash, caustic, drums.....lb. .06¼                      Potassium abietate.....lb. .06                          Acetate, kegs.....lb. .27                          Bicarbonate, gran., bbls.....lb. .10                          Bichromate, casks.....lb. .08½                          Binoxalate, bbls.....lb. .23                          Bromide.....lb. .31                          Carbonate, 80-85%, calc., casks.....lb. .06¼                          Chlorate, cryst., kegs.....lb. .09¼                          Chloride, crystals, bbls.....lb. .04                          Cyanide, cases.....lb. .55                 </p> </div>	<div style="font-size: small;"> <p>                     Meta-bisulfite, bbls.....lb. .15                      Muriate, fert., bulk, per K<sub>2</sub>O unit......50                      Permanganate, drums.....lb. .18½                      Prussiate, red, casks.....lb. .35                          Yellow, casks.....lb. .16                          Titanium oxalate, bbls.....lb. .32                      Pyridine, drums.....gal. 1.30                      Pyrocatechin, c. p., drums.....lb. 2.15                      Resorcinol, tech., kegs.....lb. .75                      Rochelle salt, bbls., U. S. P.....lb. .14                      R salt, bbls.....lb. .52                      Saccharin, cans.....lb. 1.70                      Salt cake, bulk.....ton 13.00                      Saltpeter, gran., bbls.....lb. .06                      Silica, ref., bags.....ton 22.00                      Silver nitrate, 16-oz. bot.....oz. .33                      Soda, ash, 58%, light, bags, contract,                          wks.....100 lbs. 1.23                      Soda, caustic, 76%, solid, drums,                          contract, wks.....100 lbs. 2.60                      Sodium abietate, drums.....lb. .08                      Acetate, flake, bbls.....lb. .04½                      Alginate, drums.....lb. .64                      Benzoate, bbls.....lb. .46                      Bicarbonate, bbls.....100 lbs. 1.75                      Bichromate, casks.....lb. .06½                      Bisulfite, bbls.....lb. .03¼                      Bromide, bbls., U. S. P.....lb. .31                      Chlorate, cryst., bags.....lb. .06¼                      Chloride, bags.....ton 12.00                      Cyanide, cases.....lb. .15¾                      Fluoride, bbls.....lb. .07¾                      Metallic, drums, 12¼-lb. bricks.....lb. .19                      Metasilicate, cryst.....100 lbs. 2.75                      Metasilicate, gran., bbls.....100 lbs. 2.15                      Naphthenate, drums.....lb. .09                      Naphthionate, bbls.....lb. .52                      Nitrate, crude, bulk, N. Y.....ton 25.50                      Nitrite, bbls.....lb. .071                      Perborate, bbls.....lb. .14¼                      Peroxide, cases.....lb. .20                      Phosphate, disodium, bags.....100 lbs. 1.70                      Phosphate, trisodium, bbls.....100 lbs. 2.05                      Picramate, kegs.....lb. .65                      Prussiate, bbls.....lb. .10                      Silicate, drums, tanks, 40°.....100 lbs. 80                      Silicofluoride, bbls.....lb. .06½                      Stannate, drums.....lb. .34½                      Sulfate, anhyd., bbls.....100 lbs. 1.45                      Sulfide, cryst., bbls.....lb. .02½                          Solid, 60°.....lb. .03                      Sulfoyanide, bbls.....lb. .28                      Thiosulfate, reg., cryst., bbls.....lb. .024                      Tungstate, kegs.....lb. .85                      Strontium carbonate, tech., bbls.....lb. .07¼                      Nitrate, bbls.....lb. .08                      Peroxide, 100-lb. drums.....lb. 1.25                      Sulfur, bulk, mines, wks.....ton 18.00                      Sulfur chloride, red, drums.....lb. .05                          Yellow, drums.....lb. .03½                      Sulfur dioxide, commercial, oyl.....lb. .07                      Sulfuryl chloride, drums.....lb. .10                      Tetrachlorethane, 50-gal. drums.....lb. .08¼                      Thiocarbonyl, bbls.....lb. .20                      Tin.....lb. .52¾                      Tin tetrachloride, anhydrous, drums,                          bbls.....lb. .26¼                          Oxide, bbls.....lb. .52                      Titanium dioxide, bbls., wks.....lb. 16¼                      Toluene, tanks.....gal. .30                      Triamylamine, drums, wks.....lb. 1.25                      Triamyl borate, l. c. l., drs., wks.....lb. .27                      Tribromophenol, cases.....lb. 1.10                      Trichloroethylene, drums, wks., frt.                          allowed.....lb. .089                      Triethanolamine, drums, wks., frt.                          allowed.....lb. .26                      Trihydroxyethylamine oleate,                          drums.....lb. .40                          Stearate.....lb. .35                      Triphenylguanidine, drums.....lb. .58                      Triphenyl phosphate, bbls.....lb. .37                      Tungsten, powder.....lb. 1.65                      Urea, crystals.....lb. .0475                      Vinyl chloride, 16-lb. cylinders.....lb. 1.00                      Whiting, bags.....ton 7.00                      Xylene, 10°, tanks, wks.....gal. .30                      Xylidine, drums.....lb. .36                      Zinc, metal, E. St. Louis.....100 lbs. 5.15                      Zinc ammonium chloride, bbls.....lb. .0465                          Chloride, granulated, drums.....lb. .05                          Oxide, Amer., bbls.....lb. .05¼                          Perborate, 100-lb. drums.....lb. 1.25                          Peroxide, 100-lb. drums.....lb. 1.25                          Stearate, bbls.....lb. .20                      Zinc dust, bbls., c/l.....lb. .0705                 </p> </div>
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