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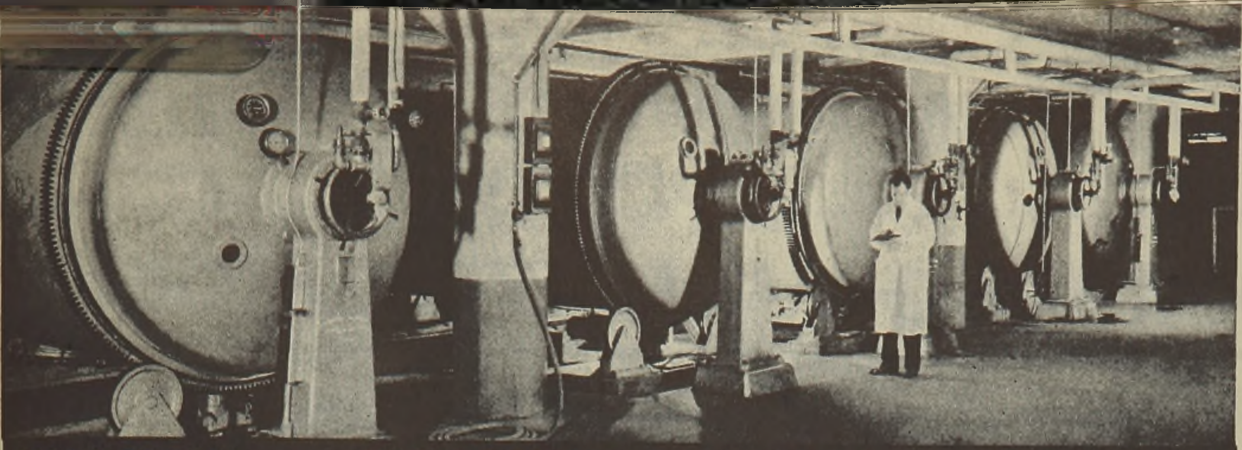

The photograph shows stainless steel mold incubation drums at the plant of Frederick Stearns & Company (see article, page 521).

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# INDUSTRIAL AND ENGINEERING CHEMISTRY
# REPORTS
# ON THE CHEMICAL WORLD TODAY

## Commerce and Industry

**Phthalic Anhydride Expansion.** Surplus phenol supplies at the close of World War I was a matter of concern to its manufacturers and the Government. The allies had besieged the chemical industry to expand phenol production by every means possible in order to meet requirements for trinitrophenol (TNP). As a result, a huge stock pile of 40 million pounds loomed menacingly over the market when hostilities ceased, and there was no synthetic organic chemical industry to absorb so much phenol. Prices dropped precipitously, from somewhere above 50 cents a pound all the way to around 8 cents.

To Monsanto Chemical Company went the unenviable task of disposing, in the best way it could, of this 40 million pounds in a market which annually got along nicely on 2.5 to 3 million. Contrary to all prognostications of economists and market experts, the phenol surplus was sold, and in a surprisingly short time. A new postwar industry, or rather two new industries (radio and phenol-formaldehyde plastics), had supplied the answer.

A parallel now seems to be developing in one of phenol's distant chemical relatives, phthalic anhydride; military demands have been greatly inflated to meet essential requirements in phthalic coatings for Army and Navy equipment and phthalate plasticizers. We have built up an enormous manufacturing capacity in phthalic anhydride as a wartime necessity, and as in the case of phenol, we will need new peacetime outlets for these facilities.

At a recent meeting of the Industry Advisory Committee and the War Production Board, it was brought out that phthalic anhydride production will soon rise to an annual rate of about 190 million pounds after having attained an annual output rate of 126 million in the first quarter of 1945. An idea of the capacity expansion in phthalic will be better obtained by contrasting these figures with normal peacetime needs. In 1929 production amounted to 9,168,946 pounds; in 1939, after normal peacetime growth in organic chemical processes and resin coatings, the output had risen to 44,274,430. In addition to phthalic anhydride's use in alkyd resins and plasticizers, the naphthalene derivative has some older established outlets, principally in the manufacture of dyestuffs, pharmaceuticals, bases for perfumes, and denaturing materials for ethanol.

These outlets will probably be widened for phthalic anhydride in the great industrial era which lies ahead. However, it would be groundless optimism to expect these normal prewar outlets to absorb the full production of present and projected phthalic anhydride facilities. The question which arises, therefore, is obvious: What new channels of trade present themselves to its suppliers? We cannot overlook the possibility that some new industry will rise, as happened in the instance of phenol, to absorb 190 million pounds or more of phthalic anhydride a year.

We must not expect that another combination of Leo Baekeland, phenolic resin, and radio will appear to solve the problem. Instead, we may have to depend upon some of the newer and promising applications to provide a market for part of the wartime increase in phthalic. One promising item in this group is dimethyl insect repellent, demand for which has been heavy enough to contribute to the over-all shortage of both phthalic anhydride and its raw material, naphthalene. Indirect or end uses undoubtedly will be found in the postwar world.

**Shifting Sources for Rayon.** The marked change which has taken place in cellulose consumption for the manufacture of rayon is one of those economic unpredictables born of wartime shortages. The prewar use of wood pulp cellulose became firmly established as a raw material for this purpose, especially by viscose rayon plants. The percentage of wood pulp in all cellulose used rose from 58% in 1932 to 85% in 1942. The other cellulose base for this purpose, cotton linters pulp, in that same period dropped from 42 to 15%. The use of both raw materials expanded along with rayon production.

The economic dogma that demand always flows into the low-cost channels still holds, but the war appears to have temporarily thrown that idea, and some others like it, out of the window. The growing consumption of chemical wood pulp in rayon manufacture during 1932–42 grew out of a need for reducing production costs. At the same time special properties of wood pulp for its use in viscose rayon were improved. In 1942 the alpha-cellulose content of wood pulp for this purpose had been brought up to a range of 88–92%. Now the trend is reversing itself.

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*An interpretative monthly digest for chemists, chemical engineers, and executives in the chemical producing and chemical consuming industries*

Consumption of cellulose by the rayon industry in this country last year set an all-time high of 367,000 short tons, and the greatest increase by far was shown by cotton linters pulp. The expansion amounted to 47.7%, or from 55,500 tons in 1943 to 82,000 in 1944. At the same time, wood pulp consumption rose by only 1.4%, or from 281,000 to 285,000 tons. The explanation for this reversal of position is dual. Labor shortages and other war difficulties have prevented the wood pulp industry from increasing production, and as a result, supplies of high alpha pulp have become exceedingly tight. The second cause, however, is the one which will bear watching. The military tire program, based largely on the use of synthetic rubber, calls for large quantities of high-tenacity rayon, and we are told that several important rayon producers favor the use of linters pulp for this purpose. In some rayon plants it is combined with wood pulp. The latter is also being used as such in the processing of high-tenacity yarn required for tire cord.

Both materials will be drawn upon heavily to meet the requirements of the tire program, and indications are that the increase in rayon's cellulose supplies will have to be met by the chemical cotton product. The Rubber Bureau's program calls for the production of 245,000,000 pounds of rayon tire cord this year, and 296,000,000 in 1946; although the recent European victory may modify these estimates, the required increase in rayon production over last year will be large.

The extent to which cotton cellulose can be applied has a limit imposed by the linters supply. A major use in recent years has been the manufacture of cellulose acetate (28.6% in 1941 against 9% in 1929). The viscose industry accounts for something less than 11% of cotton linters consumption; nitrocellulose, over 53%; cuprammonium rayon and miscellaneous, about 7.5%. The chemical cotton plants supplying this form of cellulose for the foregoing uses probably were not projected with a view to meeting additional extraordinary demands for rayon cord manufacture.

**Fertilizer's Future.** Headaches are multiplying in the fertilizer field, and like the man waiting for the other shoe to drop, the industry will not rest easy until some disposition is made of government nitrogen plants. Not only is American industry suffering from the jitters, but the Chilean nitrate organizations are also wondering whether the intentions of the Government are "honorable" to Senorita Chile.

The latest development is the State Department release concerning the conference at Mexico City, which stated that the disposition of the plants would be discussed with the Chilean Government, if such disposition had any effect on the production or export of nitrate from Chile. Plaintively the American and the Chilean groups are crying, "What is the United States Government going to do with the nitrogen plants?" More plans are going around Washington for the disposition or utilization of these units than there are "fleas on a houn' dawg".

Recently amendment S. 55 to the Independent Offices Appropriations Bill met defeat. This would have provided $3,000,000 toward the construction, by TVA, of a superphosphate plant near Mobile, Ala.

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Apparently the feeling of Congress is against the Government's entering the fertilizer business, and for that reason it appears that another fertilizer measure, Senate Bill 882, will not come out of committee. This bill provides that the Government expand its nitrogen capacity and set up in every county an average of seventy-five experimental farms for the use of fertilizers made in government plants. Indignation over this measure in fertilizer circles is running high, and many feel that it is the first step toward socialization of industry. The proposed experimental farms, if carried out, would number more than 200,000.

The legislators' idea that the farmer needs assistance in fertilizers is interesting in view of the facts obtained by The National Fertilizer Association on the practices that farmers will be following in the future. This organization asked the farmers of the Nation several pertinent questions, and the replies indicate that the messages of educational programs have been heeded. In answer to the question as to whether less money would be spent for fertilizers if farm prices declined moderately after the war, 96% of the farmers said they would not spend less, 84% are applying more fertilizer now than before the war, 70% said they would spend more for fertilizers next year, and 98% endorsed the treatment and services of the present fertilizer dealers. Even under the stringency of war, 59% said they were able to get as much fertilizer as they wanted this year.

In view of this record it is doubtful if Congress will make any radical disposition of the nitrogen plants at this time.

**Federal Finance.** Public indebtedness is of far-reaching importance, and the following from the report of the Secretary of the Treasury should interest the chemical profession. Eighty-nine billion dollars will be spent this year on the war, 10.7 billion on other government expenditures. Receipts will be about 45.7 billion, the deficit amounting to 54 billion. Debt interest will amount to 3.8 billion. In 1945 the total of goods and services in the United States will amount to 198 billion, and of this amount government expenditures will be equal to 50% and federal receipts to 23%.

Several interesting conclusions stand out. One is that the income of the Nation, as represented by the total goods and services, seems to be stabilized at about 200 billion. Another is the statement of the Secretary that postwar expenditures will be "far higher than prewar expenditures and we should plan to reduce the debt as rapidly as economic considerations permit". The problem that faces the Nation in regard to the debt is well expressed in the summation by Secretary Morgenthau that the "premature relaxation of our efforts on the tax front might jeopardize the continuing success of the economic stabilization program ...... too great a delay in adjusting the tax structure and rates might jeopardize the postwar maintenance of high levels of employment and business activity".

Last and most important, the expenditures for the interest payment on the debt amount to only 2% of the Nation's total goods and services. This low rate of interest is true only if the income of the Nation is large, and our postwar economic health depends on keeping it large.

*(Continued on page 12)*

# I. & E. C. Reports on the Chemical World Today

## *Washington*

**Sugar for Industry.** When sugar bowls begin to disappear from tables, industry has as much reason to be concerned as the housewife. Sugar of all types is an important raw material in the manufacture of drugs, pharmaceuticals, and chemicals, and such utilization has increased in recent years. Processes for the manufacture of citric acid, sorbitol, and ascorbic acid are dependent upon sugar in its different forms. These uses and the requirements of the beverage and candy manufacturers make up a sizable tonnage of sugar annually.

When domestic production and importation of sugar fall below national requirements, industry at times is forced to resort to substitutes, such as honey or maltose and dextrose. This year, however, the supply of substitutes is also limited.

The sugar estimates for 1945 thus far are not encouraging. The War Food Administration's Sugar Section stated in May that the Nation's available supplies will amount to 7,696,000 short tons, raw value, of which 5,000,000 are being allocated for civilian use (industry and household), and 1,529,000 to our allies. This indicates that 1,167,000 tons will be made available for the armed forces. It also indicates a decrease of 1,000,000 tons for civilians based on 1944 allocations. This WFA estimate, however, was predicated on the expectation of a Cuban crop of 4,100,000 tons. Since then all but a few of Cuba's 160 mills have finished grinding the 1944–1945 crop, and the trade has learned that it will amount to only 3,868,000 tons or some 232,000 tons less than anticipated. Cuba, Puerto Rico, and our domestic cane and beet growing areas comprise the principal sugar sources. If the Philippines and Hawaii could return to normal sugar production, our worries would be over.

The House Food Committee, which investigated the situation, was told that cane allotments to expanding Cuban refineries were doubled this year. At the same time United States refineries are operating at less than capacity. In Puerto Rico a prolonged drought is affecting both the current and the new crops. The sugar crisis nevertheless was laid at the door of the Commodity Credit Corporation "for failure to encourage production in Puerto Rico and Cuba, where 60% of our supply is grown". The committee recommended a "czar" to coordinate the activities of twenty-two federal agencies in sugar control and urged that negotiations begin at once for acquiring the 1946 Cuban and Puerto Rican crops.

Price policies, indirectly, are involved as well, and an industry witness told the committee that the present price of 3.10 cents per pound f.o.b. Cuba, which the CCC is paying for the 1945 crop, is the other extreme to the situation in the first World War when the Government refused to pay an offered price of 6.50 cents although the raw sugar market at the time was more than 20 cents.

Here at home the growth of other more profitable crops by beet and cane growers has been at the expense of sugar, and some believe that the Government should have discouraged this by offering better incentive payments for the growth of sugar. The normal annual output of domestic sugar as a result has dropped from 1,800,000 tons to around 1,100,000 tons, and evidently nothing can be done to correct the situation this year.

(*Continued on page 14*)

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# I. & E. C. Reports on the Chemical World Today

## *Technology*

**Synthetic Reclaim.** No one ever accused the chemist of running away from trouble, including that of his own making. When technology created a synthetic rubber industry within two years, it brought on several other problems, any one of which would normally constitute a major difficulty. The rubber manufacturing industry had been so geared to the use of natural Hevea plantation crude that new processes had to be devised for milling and compounding the synthetics. Tires of synthetic, especially heavy-duty and military types, demanded high-tenacity rayon cord, heavy loadings of carbon black, and new capacity to provide these materials.

Now comes synthetic reclaim to show that some of our past troubles were only preliminary. Reclaim is not just a conservation product. It has peculiar properties which render it an essential ingredient in compounding; even in normal times we have consumed as much as 200,000 to 300,000 tons a year in the manufacture of many articles, including tires. Most of the reclaim formerly came from natural plantation rubber, and processes for obtaining it from scrap were more or less stabilized, from the scrap dealer's yard to the reclaiming plant.

Reclaiming synthetic rubber, on the other hnad, is a complex procedure which challenges the rubber technologist. He has not just one type of synthetic to deal with but several. This may mean the development of different procedures for recovering each type. Chemicals, solvents, and oils which may be suitable for one synthetic are unsuited for another. Technologists mention a number of complex organic materials which appear particularly effective for reclaiming GR-S, such as dihydroxyarylsulfides, mercaptans, and hydrazines; however, at this stage the cost of such organic chemicals is high compared with the common reclaim oils and solvents, coal tar, naphtha, and others, which sufficed for plantation rubber.

It is possible that present reclaim equipment can be used without cellar-to-roof alteration. A leading technologist says this is the case for GR-S now available as scrap, after changes have been made in time and temperature cycles. But the identification, grading, and sorting of synthetics is something else again. It could not now be carried out except for the designations required on manufactured goods, when GR-S is used, in accordance with War Production Board regulations. Chemical tests have been worked out to assist in identifying the various synthetics in rubber scrap, and some are said to be successful. A solution of this difficult problem would constitute an important contribution. A manufacturer of articles requiring the special properties of neoprene, to cite one specific instance, will not be able to use neoprene reclaim if he finds that it is contaminated with deteriorating materials.

Reclaim research may have to be reoriented along the line of developing outstanding properties in synthetic reclaims for special applications. This goal will require additional refinement of reclaim processes and a practicable system of sorting and collecting scrap. Cost will be the dominating consideration.

(*Continued on page 18*)

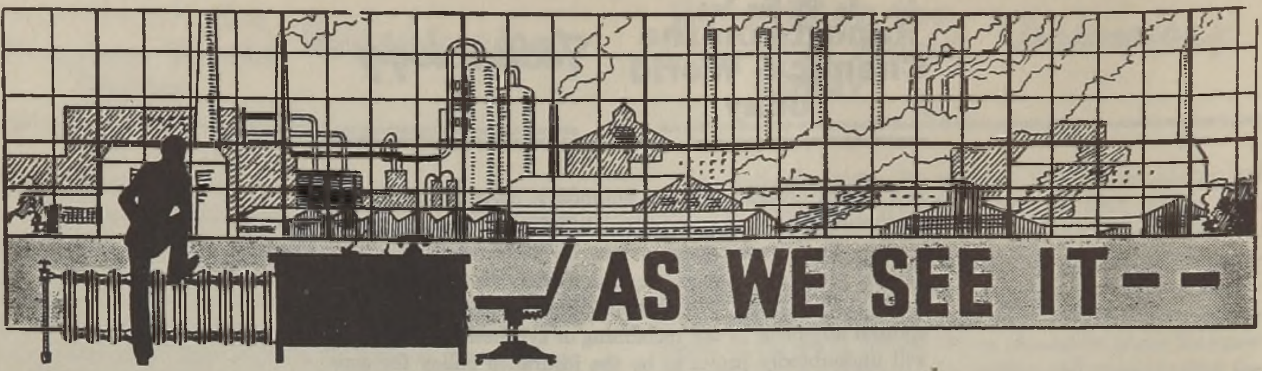
The entire program will be nullified if costs and prices of synthetic reclaims are permitted to advance to unworkable levels. The development should be accelerated, as crude natural reclaim is vanishing and none may be available over the next two years. The Rubber Bureau states that the substantial advances in the reclaiming of synthetic rubber scrap will undoubtedly prove to be the insurance policy for continued operations in this field. Some 16,000 tons of reclaim a month have been sufficient to meet demand, but now this must be increased to around 25,000 tons, or only 1000 tons a month below the highest tonnage figure ever achieved in this industry.

**Protecting Pipe Lines.** Research and field tests conducted by the magnesium industry to develop "cathodic protection" for underground pipe lines has evidently proved fruitful. In a recent discussion on postwar chemical outlets, Willard H. Dow said that this new technique of combating corrosion in industry might absorb as much as 60,000,000 pounds of magnesium annually, an amount which is some 10,000,000 pounds in excess of the Dow Chemical Company's output.

The magnesium for this purpose serves in the form of an expendable alloy anode. A number of these are installed in the soil adjacent to the pipe line to be protected, and then connected to the line. The earth around and above the anodes is conditioned by mixing with a backfill, the composition of which will vary in accordance with soil resistivities. For low-resistance soils Aquagel and ground hydrated gypsum ($CaSO_4.2H_2O$) are employed, and for high-resistance soils Aquagel, anhydrous sodium sulfate, and hydrated gypsum are utilized.

Basically, cathodic protection against corrosion is not new as Sir Humphrey Davy, over a century ago outlined a similar idea for protecting the copper sheathing then used on ships. It rests on the fact that corrosion of metal surfaces underground is an electrolytic action. Portions of the surface act like anodes and corrode; other areas behave after the fashion of cathodes and are unaffected. Earth or water surrounding pipe lines acts as an electrolyte, and current flows from anodic to cathodic areas. By transferring this action to an "expendable" and replaceable anode in the earth, destruction of the pipe line or other structure through corrosion is either greatly reduced or eliminated.

Magnesium, in proper balance with other metals, is said by Dow engineers to be highly desirable for an expendable anode. It has driving voltage to protected steel (against a copper sulfate reference electrode) of 0.7 to 0.8 volt, and shows no tendency to polarization. The composition of the alloy, on the basis of their latest reports, evidently is important. The anode now offered to industry for this purpose is a controlled composition in which the iron and nickel content is held to less than 0.003%. In one typical field installation total current output was only 10 amperes, an average output of about 37 milliamperes per anode.



An array of varied articles awaits you this month. Departing from the custom, followed this year, of making symposia a feature, we present an issue of varied discussions. We wonder if the reader has noticed the quality of the symposia already published in 1945. It speaks well for ACS membership and for intellectual writing qualities of chemists and chemical engineers of the Society. In the five issues of 1945, papers from six symposia were presented.

This month we begin with the subject of cracking paraffins. Greensfelder and Voge, of Shell Development Company, present the first of a series of articles to appear in *I. & E. C.* on the catalytic cracking of pure hydrocarbons. This time Greensfelder is examining the cracking of paraffins, ranging from propane to wax, and using a silica-zirconia-alumina catalyst. The authors note that there is a selective manner in which the carbon-carbon bond ruptures, and that the use of catalytic cracking methods is five to sixty times as rapid as thermal cracking.

Microbial Amylase Preparations is the awesome title of paper No. 2. An amylase is an enzyme that acts as a saccharification agent for starches. Therefore a microbial amylase is an enzyme that has its origin in a microorganism. The authors, Lu Cheng Hao and John Jump, come from that little scientific "League of Nations"—the Joseph E. Seagram & Sons' training school. Hao and Jump find that, compared to malt as a starch saccharification agent, the mold amylase is far more efficient on a weight basis. The uncompromising rules of economics, however, must be considered, and price is at present a deterring factor. Yet it is on such problems that chemistry forages and grows fat.

Polythene is a new generic term, the gift of du Pont and Imperial Chemical Industries. It is also a new plastic; in fact, the name connotes those polymers of ethylene suitable for plastics. Hahn, Macht, and Fletcher, of the du Pont organization, present an extensive article on the new material, and examine its properties and characteristics. One of the important uses for this latest of the plastics is insulation for electrical equipment, and as such has had a varied and useful life in the Army and Navy.

Molasses stillage is a problem in applied chemical economics. As far as the mechanics of the disposal operations of this waste material go, the solution has already been found. Facing the sugar manufacturers, however, is the question of what to do with it once it has been mechanically processed. Reich, of Pennsylvania Sugar Company, airs these difficulties this month. Going even farther, he discloses the results of low-temperature carbonization of stillage in a new furnace. The results of the low-temperature technique are varied according to the chemical conditions of the stillage fed to the furnace. Properties can be changed from hard to soft, dense to porous. End product can serve as a chicken feed or a wood charcoal substitute.

Pickling liquor is a major waste disposal problem to certain industrial areas in the United States. This month we carry another contribution on the subject by one of our foremost experts, W. W. Hodge; with Hoak and Lewis of Mellon Institute of Industrial Research, he examines the treatment of these liquors with limestone and lime. Considerable savings are found possible with this combination.

Mixing in high-pressure autoclaves is a necessary chemical operation, and the means of its doing are many. However there is always room for improvement; Kiebler, of Carnegie Tech, adequately describes how it was accomplished in coal research experiments. Pressures went as high as 6000 pounds per square inch, and the stirrer attained about 120 r.p.m.

Two papers from the Symposium on Catalysis in the Petroleum Industry are included in this issue; other articles from this group were printed in April. Thomas, of Universal Oil Products Company, writes on Reactions of Hydrocarbons in the Presence of Cracking Catalysts, with special emphasis on olefins. Ardern, Newton, and Barcus, of Houdry Process Corporation, author a paper on Catalytic Cracking of Cuts from Coastal Crude; "cute chemical congeneracy", comment we on the title. The authors use a silica-alumina catalyst on four narrow-boiling fractions from Coastal crude. A great deal of the paper is given over to determining the results of varied severity of cracking.

The gradual but certain depletion of high-rank Appalachian coking coal will some day create knotty problems. For manufacturers in the Midwest these problems almost became current as a result of the transportation shortage. Relief could be obtained by using Illinois coal, which has a higher moisture content than the regular eastern grade. In order to experiment with this type of coal, Reed, Jackman, and Henline built a slot-type oven which, according to the results, exactly duplicates commercial units.

If the Nation ever exhausts its petroleum fuels, ethyl alcohol is waiting to take their place; we need not worry over the proper antiknock agent—it has already been tested. Pitesky and Wiebe, of Northern Regional Research Laboratory, give an extensive report on the use of iron pentacarbonyl, $Fe(CO)_5$, as an antiknocker in alcohol. However, it has other important uses that will probably be realized before the Nation is forced to utilize such a substitute fuel. Tropical countries are seriously considering it as a substitute in wartime, and many of the farm organizations are already sponsoring it. Norelli and Gard, of Westinghouse Electric & Manufacturing Company, write of their experiments in determining the effect of temperature on the strength of phenolic laminates.

***With the Departments.*** Munch, our instrumentation specialist, starts his column this month with a brief analysis of postwar business, then considers means of determining sodium and potassium. He also covers the remote recording of pressure and a new gas analyzer. Brown will cover in two installments the modern methods of measuring small differences—techniques worked out by the mechanical industries and well worth knowing by the chemical fraternity. Von Pechmann is tackling an old bugaboo of the chemical field, waste due to carelessness of workers. Methods of preventing the wrong measurement and mixing of chemicals are discussed.

F. S. Van Antwerpen

INDUSTRIAL AND ENGINEERING CHEMISTRY
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# Editorials

WALTER J. MURPHY, EDITOR

## Summer Course Chemists?

RECENTLY a technical journal published by one of our better known scientific schools carried the following interesting news item:

> Miss — had been working in the industry for only two months before she enrolled for the training and found it of great value for orienting her for her work.
>
> Nor was this the young laboratory technician's first experience at —. After her graduation from — high school in 1943, she enrolled in one of — 's war training courses in industrial chemistry.
>
> After only one summer course, Miss — stepped right into a position as *chemist* for the — laboratory at — company.

A statement of this kind is one which the chemical profession deplores because of its tendency to convince the lay public that a chemist can be produced by "one summer course". Particularly disheartening is the realization that such a misleading statement appears in the publication of an institution that is engaged in the training of chemists and chemical engineers.

The readers of Industrial and Engineering Chemistry are well acquainted with our efforts to obtain full and proper recognition of the profession. It is inexcusable for any institution to publish an erroneous statement conveying the idea that chemists can be trained in "one summer course" following a high school education. For good and sufficient reasons, we must differentiate between laboratory technicians on the one hand and chemists and chemical engineers on the other. The news item quoted is a distinct backward step in the program of educating the public as to what constitutes a chemist or chemical engineer. It is the duty of each member of our profession to protest when material of this type appears.

## Developing Esprit de Corps

WEBSTER'S New International Dictionary defines esprit de corps as "the common spirit pervading the members of a body or association of persons. It implies sympathy, enthusiasm, devotion, and jealous regard for the honor of the body as a whole".

Esprit de corps is a rather subtle emotion; it usually results not from one but from a combination of many different factors. One of the principal reasons why armies, from time immemorial, have worn uniforms, insignia, and decorations, is to assist in the development of an esprit de corps.

Strangely enough, but a relatively small percentage of American Chemical Society members now wear the ACS identification pin. With a national and international membership of well over 40,000, and with a large segment traveling extensively, it is highly desirable that pins be worn.

Recently your Editor was traveling on the *Twin Zephyr* from Minneapolis to Chicago when a young man occupying the seat opposite asked if he might borrow a magazine. Noting the ACS lapel button, he mentioned that he, too, was a member of the Society. What would have been a rather dull and uninteresting trip was transformed into an entertaining, and it is hoped, mutually profitable experience.

Again and again, while traveling, your Editor has been able to meet a number of chemists and chemical engineers, many of them Society members, simply because they were wearing the identifying insignia of the Chemical Warfare Service. An ACS button would accomplish the same desirable result in the case of civilians. Let's tell the world we are proud to be members of the American Chemical Society. Let's identify ourselves as Society members.

If chemists and chemical engineers expect the public to think of them as members of a profession, they must first learn to do the many things that make for an intense, live esprit de corps.

## Roosevelt on Science

THE following excerpt is from the last speech prepared by our late President, Franklin Delano Roosevelt, shortly before his untimely and tragic death, and was to be delivered, via the radio, to those who were to attend the 350th Jefferson Day dinners. It is of special significance to scientists, and a direct challenge to them to contribute more of their time, energies, and abilities to the solutions of moral, economic, and political problems:

> Thomas Jefferson, himself a distinguished scientist, once spoke of "the brotherly spirit of science, which unites into one family all its votaries of whatever grade, and however widely dispersed throughout the different quarters of the globe".
>
> Today science has brought all the different quarters of the globe so close together that it is impossible to isolate them one from another.
>
> Today we are faced with the preëminent fact that, if civilization is to survive, we must cultivate the science of human relationships—the ability of all peoples, of all kinds, to live together and work together, in the same world, at peace.

## Sensible Suggestion

CHARLES E. WILSON, president of General Electric Company and formerly executive vice chairman of the War Production Board, has, in the *Saturday Evening Post* for May 5, examined carefully our war economy. His theme is to show the American public that we will get something out of the war in the form of scientific development. Most of the inventions described are familiar to the readers of INDUSTRIAL AND ENGINEERING CHEMISTRY and need no repetition here. Wilson admits the importance of these developments, but he sees other dividends that we, as a nation, will gain from the war. One of the most important, he thinks, is the demonstration that industry and government can cooperate. This is an advantage that is very welcome to business and that should not be lost in the postwar. Wilson hopes that cooperation will be extended indefinitely to a continuing project of preparedness. However, for a preparedness program we need research organizations, and he suggests that some of the work of the Office of Scientific Research and Development be extended into a long-range program. Other governmental organizations, such as the Naval Research Laboratory, the Air Force Laboratories, the ordnance laboratories and proving grounds, and Chemical Warfare Service, should be maintained. But he emphasizes that their usefulness would be increased and their outlook broadened if they were provided with competent civilian advisory committees. The chairmen would work with high-ranking officers and, as such, would constitute a small general-staff group to keep the armed forces abreast of scientific changes. This plan has our full approval. From the number of suggestions it is certain that the postwar will see the adoption of some such plan. The present scientific offices have paid off their original investment as far as war improvements are concerned. If we are to remain scientifically strong and well prepared for any emergency, we must incorporate the brains and abilities of scientists into the armed forces. There is a common complaint that the general staff always prepares to fight the last war; if, unfortunately, there is to be a "next war", the utmost of our resources should be applied during peace to the task of keeping the Nation alert and able to meet the danger.

## What Price Reviewing?

THE hundreds of chemists and chemical engineers who gratuitously give of their time, energy, and abilities in the role of reviewers of manuscripts offered for publication in AMERICAN CHEMICAL SOCIETY journals deserve unstinted praise for the important service they render the journals, the SOCIETY, and science. Quite frequently for perfectly good reasons they remain anonymous and therefore cannot receive the credit due them and the personal thanks of the authors whom they have assisted.

One of the many pleasant discoveries made by your Editor when he came to Washington about two years ago was the very cordial relationships which usually develop between author and reviewer. The highly ethical approach of reviewers evaluating manuscripts is a credit to our profession; similarly, the receptive attitude of authors to many of the suggestions made by reviewers, even though such suggestions are not always accepted, and in this connection we wish to reiterate the statement which we make so frequently to authors that they are not obliged to accept suggestions of reviewers unless they are fully in accord.

Very infrequently, however, we do have a clash of personalities and misunderstandings, and we present the following comments from a reviewer with the idea of improving still further a very satisfactory state of affairs:

> It seems to me that a reviewer should make certain not only that the data presented are of a worthwhile nature, but he should also help the prospective contributor to present these data in the best possible way. An important point in this connection is proper "labeling of the goods". Young authors usually make the mistake of using too inclusive a label, when a specific label would do more justice to the author and would avoid disappointing the reader. Often a subtitle may be used for this purpose. A general title should involve the responsibility of coordinating one's contribution with all important data and concepts available on the subject matter.
>
> I feel that any doubt which presents itself to the reviewer on perusing a manuscript should be taken very seriously by the author. The reviewer is usually an expert in the specific field. If this expert has difficulty in understanding just what the author is driving at, how much more difficulty will the general reader have? In helping to clear up this doubt the reviewer is really doing a service to the author, and while he expects no gratitude, at least he does not like to be barked at. Any intelligent author will see this point. Those who bark lay themselves open to the suspicion that they are either not intelligent or that they want to hide something by barking. It is this which casts a reflection on their work; not the suggestions made by the reviewer. In some cases, authors have made the suggested changes but have still barked against the reviewer . . . reviewers are usually very busy people and like to have their efforts appreciated just like other mortals.

And while on this general subject we add the viewpoint of still another reviewer who writes us as follows:

> The average paper contains an introduction, some review of the pertinent literature, a description of materials and methods used, and a list of references. Such "overhead" items often use up a good share of the total space occupied by the paper, but are, of themselves, no contribution. Along with them there is the real meat of the article—the new facts and data which have been uncovered. To save space, the ratio of "meat" to "overhead" should be increased, but there seems to be a distinct tendency for just the opposite to happen. I can cite many older papers (and some modern ones too of course) which could easily have been written up as a dozen or more separate articles if their authors had chosen to do so.
>
> Many present-day workers unfortunately seem to feel it necessary to present each minor advance in the study of a large problem in the form of a paper, whereas three or four similar advances perhaps could just as well have been published at one time and the paper would have been only a little longer. The step-by-step method of publishing actually lays an even greater strain on our facilities, because not infrequently the first conclusion, in the light of later work, is seen to have been in error. Still more papers then have to be published (frequently from other laboratories as well as from the original one) merely to get the record back to the place where it was before the original error was put out.

Since our "reviewer corps" is recruited mainly, if not wholly, from authors, we do not believe there will be many who will disagree with these remarks.

## Professional Advancement

THE values of life and work never change, either for chemists, chemical engineers, or members of the professions of the children's poem, "Doctor, Lawyer, Indian Chief". Below are words of advice that, in these times of discontent, have added meaning. They are by the poet—Rudyard Kipling—who did more than any other to romanticize the men who follow science and engineering:

> If you stop to find out what your wages will be,
> And how they will clothe and feed you,
> Willie, my son, don't you go to the sea,
> For the sea will never need you.
>
> If you ask for the reason of every command,
> And argue with people about you,
> Willie, my son, don't go on the land,
> For the land will do better without you.
>
> If you stop to consider the work you have done,
> And to boast what your labor is worth, dear,
> Angels will come for you, Willie, my son,
> For you'll never be wanted on earth, dear.

In line with the concept Kipling had of the unbending, uncompromising work of the scientific professions (the group he named "the sons of Martha"), the person he described in the poem is Mary's son. The true son of Martha stoops not to complaints, but continues in his path of "simple service simply given to his own kind in their common need". No matter what the circumstances, chemistry is a profession and its practitioners are professional men. As professional men, we must learn and insist on fighting our battles in our own professional way. The results may be slow in coming, but the results obtained will be more lasting. The basis for advancement of a profession must be professional, grounded on education, training, and demonstrable facts. Our demands for greater professional recognition should be based on benefits and service given. The mass good from an industry can never accrue over any long period to one group, professional or otherwise; and if, for any period of time, either capital, labor, management, or professional factions obtain advantages not based on solid grounds, those advantages will be short-lived and will react to the future detriment of the group involved. Platitudes are easy to mouth—either pro or con—but eternal values have not been superseded by recent demonstrations of temporary economic advantages to be gained solely by mass action. In any profession the value of the professional man to the public is not increased by regimentation. Cancer will never be cured, rheumatic fever will never be conquered, by the organization and strict maintenance of a doctors' union. The cures will come through research, through work—hard, uncompromising work on the part of some individual or research team that can lose itself in a problem, some individual who can forget himself into immortality. So it is with chemistry. Industries, professional advancement, and fame will come from test tubes and laboratories, not meetings of protest or unionization; even its proponents readily admit unionization is essentially a leveling process.

One would have to be endowed with almost supernatural power to be able to correct the thousands of inequalities that exist today and that have existed since the world began. All the learned professions and a large proportion of the white-collar workers are concerned with this problem. We know of no profession in which some segment is not dissatisfied; even doctors, lawyers, and dentists are vocal on the subject. There is a strong tendency to compare shining lights, the outstanding figures, and big money-makers in other professions with the least fortunate in one's own. Many chemists and chemical engineers are in high salary brackets. So are many doctors, lawyers, and dentists. Unfortunately it is likewise true that many chemists, chemical engineers, doctors, lawyers, and dentists are not receiving adequate compensation.

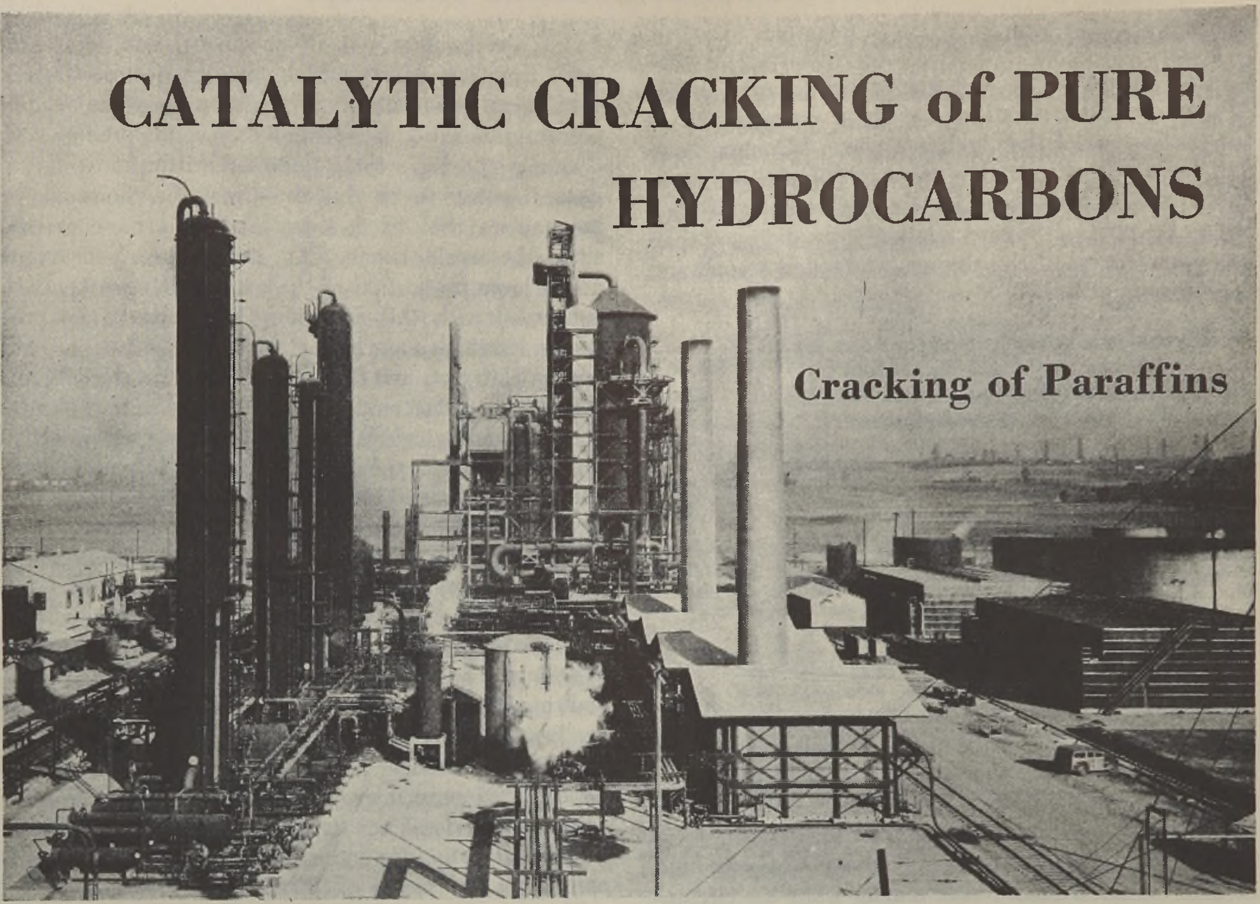
"The Federal Diary", a column appearing in *The Washington Post*, recently presented startling statistics showing that some master mechanics in our navy yards are being paid between $10,000 and $12,000 per year, including overtime. In the past several years they have earned more than members of Congress, the subcabinet, or federal boards and commissions. Indeed, the admiral who is in command of a navy yard is paid annually a base salary of $8000.

He who can correct these conditions and situations, indeed he who can provide the learned professions with a workable solution, is assured undying fame. In the meantime those who are not so gifted and talented must struggle along to improve those conditions piecemeal, on the basis of a long-range approach to a perplexing problem. Each individual can, and should, play a role, for it is still true that "God helps those who help themselves". The problem is one with many facets. Its existence is known, and the problem, far from being one thrust upon the chemists and chemical engineers just recently, has existed since the profession began. When a little band of pioneers met to form the AMERICAN CHEMICAL SOCIETY, they recognized the same problem; they chose to solve it by seeking means to improve the professional standards, by making the chemist a better equipped man to solve his everyday problems. The improvement in our profession since that day is a measure of their acumen. What is needed are workable ideas on how further progress can be achieved. Quite possibly collective bargaining, as differentiated from unionization, is another tool for the profession, but it is not the whole answer.

Better science, better literature, better selection of students, better educational requirements, better equipment will lead to a better profession, a better financial reward. Look to your working tools; by them you advance!

# CATALYTIC CRACKING of PURE HYDROCARBONS

## Cracking of Paraffins



**The behavior of paraffin hydrocarbons ranging from propane to wax was studied under catalytic cracking conditions. A silica-zirconia-alumina catalyst was used in a small, fixed-bed cracking unit. It was observed that carbon-carbon bond ruptures are selective to give fragments of three or more carbon atoms. Secondary reactions include isomerization of olefins, saturation of olefins, and production of aromatics. A comparison with thermal treatment shows catalytic cracking is five to sixty times as rapid, is accelerated more for the large than for the small paraffins, and gives considerably different products. . . . The photograph shows a Fluid Catalytic cracking plant of Shell Oil Company at Wilmington, Calif.**

B. S. GREENSFELDER AND H. H. VOGE

*Shell Development Company, Emeryville, Calif.*

CATALYTIC cracking of petroleum fractions with silica-alumina or clay catalysts has been described in the literature in terms of technical plant and commercial specifications of raw materials and products. Most of the results, however, have been obtained with petroleum oils containing a wide variety of hydrocarbons. To secure further insight into the chemistry of the process, the behavior of a number of selected pure hydrocarbons and a few special mixtures such as isododecane and Parowax under catalytic cracking conditions has been investigated. Some time ago data from the Universal Oil Products Company covering *n*-paraffins of 8 and 16 carbon atoms and *n*-olefins of 4, 5, 8, and 16 carbon atoms were published by Egloff and co-workers (*3*); recently these were supplemented by results for cyclohexene, Decalin, Tetralin, and alkylbenzenes (*1*, *17*). In our work fifty-six hydrocarbons have been used, including a wide variety of types and molecular weights, to obtain self-consistent results of broad scope.

This paper reports the results from cracking paraffin hydrocarbons. Data for olefins, naphthenes, and aromatics are to follow. Not only are hydrocarbons represented that may occur in crude oil fractions, but also the important types found in the products of catalytic cracking, so that evidence as to secondary reactions is available. Although the various hydrocarbons display great differences in behavior over the cracking catalyst, it has been possible to arrive at a few rules which cover the majority of the observations, and the results may be explained accordingly in terms of the original molecular structures and the selective activity of the catalyst. Throughout, an effort has been made to compare catalytic cracking results with thermal cracking since such comparison brings forth strongly the specific effects of the catalyst.

Thermodynamic considerations have been of little positive assistance in this work. The failure of many of the primary reactions to reach equilibrium and the prevalence of important secondary reactions make impossible any general prediction of extent of reaction or composition of product from thermodynamics.

Selection of the catalyst used in this study was made on the basis of (*a*) characteristics typical of present commercial cracking catalysts in terms of total conversion and nature of product, (*b*) use by other investigators, (*c*) reproducibility at source, and (*d*) controllable composition. Synthetic catalyst made by the Universal Oil Products Company and designated "UOP cracking catalyst, type B", met these requirements and was used throughout. Such catalysts are described in many patents—for example, several to Thomas (*16*), and the general preparative procedure has been given (*15*). The catalyst used by us was found to contain as principal components 86.2% silica, 9.4% zirconia, and 4.3% alumina, by weight, and was in the form of cylindrical pellets, 3 × 3 mm. Our experience is that the UOP-B catalyst gives results similar to those with the synthetic silica-alumina catalysts now commonly employed for commercial catalytic cracking. The silica-alumina-thoria catalyst used by Egloff and co-workers (*3*) should also give similar results.

## EXPERIMENTAL PROCEDURE

**Definitions and Terminology.** "Catalyst volume" is the total volume occupied by the loosely packed catalyst pellets, as measured in a 100-ml. graduated cylinder before charging to the reactor. "Process period" is the duration of hydrocarbon flow to reactor. "Flow rate" is given as moles of hydrocarbon input per liter of catalyst per hour. "LHSV" (liquid hourly space velocity) means the volumes of liquid input (60° F.) per volume of catalyst per hour; it is the same as "liquid throughput". "GHSV" (gas hourly space velocity) is defined as volumes of gas input (0° C. and 760 mm.) per volume of catalyst per hour. "Contact time" is computed from the average flow of gases under reaction conditions (simple average of input and output flows), assuming the catalyst volume to be entirely void. Ideal gas laws are used. In thermal runs residence times are based on hot free space. "Gas" is defined as $C_4$ and lighter, or alternatively as material boiling below 10° C. "Liquid" is material above $C_4$ or above 10° C. "Gasoline" is the fraction from 10° to 200° C. "Carbon" is the carbon in the catalyst deposit. "Total amount decomposed" or "extent of cracking" includes gas, liquid boiling below the original, and carbon, summed on a no-loss basis. "Carbon number" is the average number of carbon atoms per molecule.

**Apparatus and Procedure.** A reactor system for continuous flow experiments was used. The pressure was atmospheric, and the process period one hour, except when otherwise noted. The hydrocarbon was fed down the vertical catalyst tube, and the product was conducted through an ice-cooled condenser into a gas separator, from which gas passed to a collecting and measuring bottle and liquid to a tared, iced receiver. Gases were metered in through a rotameter. Liquids were taken from a 100-ml. buret by a Hills-McCanna pump. Hydrocarbons with melting points above room temperature were displaced by mercury from a steam-heated reservoir directly above the reactor. The input flow rates reported are averages for the hour; mean deviations for 10- and 15-minute periods were of the order of 2% of the rate.

The 18-8 chromium-nickel steel (A.I.S.I. type 302) catalyst tube was 76.5 cm. in length and 1.58 cm. in inside diameter, with a coaxial thermowell of 0.63 cm. o.d. The tube volume was 120 cc., but it was normally charged with only 50 cc. (37 cm.) of catalyst. The remainder was occupied by type 302 steel fillers for 21 cm. above and 18 cm. below the catalyst for preheating and support. In noncatalytic experiments the central section was either left empty or filled with inert material. The electric heater, 76 cm. long, had an independently controlled preheating section (9 cm., 0.35 kilowatt) and a main heating section (67 cm., 1.35 kilowatts). Variable autotransformers were used to control the temperature. Operation was manual, guided by ammeters and a continuous temperature recorder. The temperature at the center of the catalyst bed was held within 3° C. of the desired value. The temperature gradient along the catalyst bed rarely exceeded 5–10° C.

To start a run, the system was flushed with nitrogen and tested for leaks. Then the hydrocarbon was fed, usually for one hour. At the end of the processing period, the gas collecting bottle with total product gas was disconnected. A 20-minute nitrogen flush followed, with a cold trap (solid carbon dioxide) to collect hydrocarbons. The liquid receiver was then withdrawn and weighed. The cold trap was disconnected only after regeneration, and any hydrocarbon collected (usually there was none) was added to the liquid product.

**Distillation of Product.** The liquid receiver from the reactor served as the distillation kettle and thus eliminated transfer losses. A small fractionating column, 0.5 cm. i.d. × 98 cm., packed with a wire spiral, and vacuum-jacketed, was used. The theoretical plate equivalent was about ten, and holdup was small. Distillations were made with a reflux ratio of about 10 to 1. The gaseous fraction was blended with the process gas, and the composite was analyzed, usually by low-temperature distillation, so that correction could be made for $C_5$ and higher carried over with the gas. When taken, cut points for fractions were: $C_5$, 10–50° C.; $C_6$, 50–75°; $C_7$, 75–100°; $C_8$, 100–125°. Distillation losses were usually distributed over the liquid products; if they were large, they are mentioned. The boiling point curves are based on the total liquid product.

**Analyses.** Gas analyses included low-temperature distillation with sulfuric acid absorption of fractions, or the latter type of absorption and combustion. Molecular weights were computed from the distribution of components or from combustion analysis, or were measured by the efflux method. Hydrogen was determined by the shrinkage on passing the sample with excess ethylene over nickel catalyst. All gas analyses were computed to an air-free basis at 0° C. and 760 mm.

Olefin contents of liquid fractions are based on Rosenmund bromine numbers computed to molecular weights estimated from boiling ranges. Aromatic contents are from specific dispersions, corrected for bromine number (*6*). Both olefin and aromatic contents are expressed as per cent by weight.

**Regeneration of Catalyst.** The catalyst was heated to 580–600° C., and a mixture of 300 volumes of air and 600 of nitrogen per volume of catalyst was passed in one hour. Air alone was then passed at a rate of 600 volumes per hour until the effluent gases gave no more than a slight milkiness when bubbled for 15 seconds through a clear solution of barium hydroxide. The total time for regeneration was 2–4 hours.

A single batch of catalyst was usually used for five to ten runs, with regeneration between runs. Catalyst activity tests showed that, when the regeneration was properly carried out, the restoration of original activity was complete regardless of the hydrocarbon reacted.

**Carbon Determination.** The carbon deposited in any form on the catalyst was determined from the amount of carbon dioxide produced during regeneration. In the early experiments the effluent gas was analyzed for carbon dioxide every 15 minutes by absorption in potassium hydroxide. This method neglected carbon monoxide in the gas, which amounted to 25–50% of the carbon dioxide, but it did give a relative measure of carbon deposits.

In the final method the regeneration gases were passed successively through a cold trap at −80° C. to recover liquid, a furnace containing cupric oxide at 650–700° C. to oxidize carbon monoxide to carbon dioxide, a drying tube containing anhydrous magnesium perchlorate, and a tared tube of Ascarite to absorb carbon dioxide. The carbon figures quoted were determined by this method unless indicated by a footnote in the tables.

Actually, the catalyst deposit is not strictly carbon but a coke containing up to about 8% hydrogen. Our figures refer to the carbon content of this coke, the hydrogen having been neglected.

**Hydrocarbons.** The hydrocarbons were selected for availability consistent with moderate purity. Some were synthesized. Sources and properties follow: Propane, *n*-butane, and isobutane were from Shell Oil Company, Inc.; analyses are given in Tables I, II, and III. *n*-Pentane was a fraction from straight-run gasoline, estimated to be 97% pure; the A.S.T.M. 5% and 95% distillation temperatures were 35.5° and 38.0° C., $d_4^{20}$ was 0.6266, and $n_D^{20}$ was 1.3574. *n*-Heptane was from the California Chemical Company; boiling point was 98.4° C., $d_4^{20}$ 0.6837, $n_D^{20}$ 1.3877. Iso-octane was from Rohm and Haas Company; boiling point 99.3° C., $d_4^{20}$ 0.6918, $n_D^{20}$ 1.3916. *n*-Dodecane was prepared from lauryl alcohol from Eastman Kodak Company; boiling point was 217° C., melting point −9.8° C., $d_4^{20}$ 0.7486, $n_D^{20}$ 1.4216. Isododecane was the product obtained by hydrogenating tri-isobutene from the cold-acid polymerization process. The A.S.T.M. 5% and 95% distillation temperatures were 175.8° and 178.7° C.; $d_4^{20}$ was 0.7474, $n_D^{20}$ 1.4201, and bromine number

TABLE I. CATALYTIC CRACKING OF PROPANE

(Process period 28 minutes; GHSV 186; flow rate 8.3 moles/liter/hour)

| | 500° C. | 550° C. | 600° C.[a] | Feed |
|---|---|---|---|---|
| Gaseous product, vol. % | | | | |
| $H_2$ | 0.7 | 1.1 | 2.4 | 0.3 |
| $CH_4$ | 0.5 | 0.7 | 1.5 | |
| $C_2H_4$ | 0.7 | 0.5 | 1.7 | . . . |
| $C_2H_6$ | 2.3 | 3.0 | 0.3 | 4.0 |
| $C_3H_6$ | 0.2 | 0.0 | 3.4 | . . . |
| $C_3H_8$ | 95.3 | 93.4 | 90.1 | 95.7 |
| $C_4H_8$ | 0.1 | 1.3 | 0.1 | . . . |
| $C_4H_{10}$ | 0.2 | | 0.5 | <0.3 |
| Liquid product | None | Trace | None | . . . |
| Carbon | Trace | Trace | Trace | . . . |

[a] Process period 60 minutes; feed contained no ethane.

TABLE II. CATALYTIC CRACKING OF *n*-BUTANE

(GHSV 186; flow rate 8.3 moles/liter/hour)

| | | | | |
|---|---|---|---|---|
| Temperature, ° C. | 450 | 500 | 550 | 600 |
| Process period, min. | 35 | 35 | 35 | 60 |
| Gaseous product, vol. % | | | | |
| $H_2$ | 1.0 | 2.0 | 2.2 | 3.0 |
| $CH_4$ | | | 2.0[b] | 5.8 |
| $C_2H_4$ | | | 1.1[c] | 3.6 |
| $C_2H_6$ | | | . . . | 2.1 |
| $C_3H_6$ | | | . . . | 4.3 |
| $C_3H_8$ | | | . . . | 0.3 |
| Iso-$C_4H_8$ | 0.2 | 0.0 | 0.3 | 1.0 |
| *n*-$C_4H_8$ | 0.5 | 0.5 | 2.8 | 2.3 |
| $C_4H_{10}$[a] | 98.3 | 97.5 | 91.6 | 77.6 |
| Liquid product, wt. % | None | None | None | 0.6 |
| C, % by wt. of charge | None | None | None | 0.4 |

[a] The feed contained 98% *n*-$C_4H_{10}$ and 0.5% iso-$C_4H_{10}$.
[b] Including ethane and propane.
[c] Including propylene.

(grams/100 grams) 3.9. Cetane was from du Pont; boiling point about 285° C., melting point 16.7–16.8° C., $d_4^{20}$ 0.7740, $n_D^{20}$ 1.4350. Parowax was from Socony-Vacuum Oil Company; melting point (A.S.T.M. D87–37) was 50.5° C. Fractional analysis of a similar wax is discussed in the text.

## CRACKING BEHAVIOR

Paraffins from $C_3$ to $C_{24}$ were examined. The compounds are listed in the order of increasing molecular weight. Comparisons with thermal cracking data from the literature follow the general discussion, except in the case of the dodecanes, for which our thermal experiments are more conveniently discussed in conjunction with the catalytic results. Because formation of liquid boiling above the feed was limited to a few per cent with paraffins, such higher-boiling material was not separated but was included with uncracked hydrocarbon in the material balances.

**Propane.** Table I gives the results. The amount of reaction was slight even at 600° C. It appears that the catalyst has little effect on the lowest paraffin hydrocarbons; with propane the rate of cracking, compared to thermal treatment, is increased only by a factor of 2 or 3, and the course of the reactions is not much altered.

***n*-Butane.** Normal butane was passed over the catalyst at 450° to 600° C., with the results shown in Table II. The rate was chosen to give a slightly longer residence time than that involved when cetane is cracked at 2 LHSV. Only about 1% of the butane was cracked at 500° C. and about 4% at 550° C. Thus an important conclusion is that any butane produced at these temperatures by the cracking of higher compounds will remain practically unaltered.

Products from both thermal and catalytic cracking of *n*-butane at 550° C., with a flow rate of 9.3 moles per liter per hour, were analyzed for isobutane by infrared absorption. Isobutane contents were the same as that of the charge; there was thus no isomerization. The absence of isomerization in butane pyrolysis has also been shown elsewhere (*12*); the virtual absence of catalytic isomerization is of interest in view of the prominent isobutane production when cracking higher hydrocarbons, which must have another explanation—namely, olefin isomerization followed by saturation. Data showing the validity of the latter mechanism will be given in subsequent papers.

Catalytic cracking of *n*-butane is appreciable at 600° C. and proceeds by a number of paths, including splitting to methane and propylene or to ethane and ethylene. Dehydrogenation of butane to *n*-butenes occurs to a slight extent at 550° and 600° C., but is far below that secured with dehydrogenation catalysts.

**Isobutane.** Results with isobutane (Table III) are similar to those obtained with *n*-butane. About 2% of the material was cracked at 500° C. and about 4% at 550° C. The amount of dehydrogenation was somewhat greater than with *n*-butane, parallel to thermal behavior.

***n*-Pentane.** Like the butanes, *n*-pentane cracked very little at 500° C. Results are shown in Table IV. The small volume of gas was not analyzed. The liquid recovered boiled at 35–36° C., corresponding to unchanged *n*-pentane; it could not have contained more than 1% isopentane.

***n*-Heptane.** Normal heptane cracked little at 500° C. and only 9.5% at 550° C. (Table IV). Practically no $C_5$ or $C_6$ hydrocarbons were formed; this clearly demonstrates the tendency of the catalyst to remove principally fragments of three or more carbon atoms. The gas was rich in olefins, including isobutene, and low in methane and hydrogen.

To increase the conversion, *n*-heptane was also cracked at 600° C. and a higher flow rate. Under these conditions 16% was cracked. The production of ethane and ethylene was unusually high, but there was no corresponding quantity of $C_5$ hydrocarbon. The distillation curve for the liquid product (not shown) indi-

TABLE III. CATALYTIC CRACKING OF ISOBUTANE

(GHSV 186; flow rate 8.3 moles/liter/hour)

| | | | | | |
|---|---|---|---|---|---|
| Temperature, ° C. | 450 | 500 | 550 | 600 | Feed |
| Process period, min. | 30 | 29 | 32 | 24 | |
| Gaseous product, vol. % | | | | | |
| $H_2$ | 0.4 | 0.8 | 1.9 | 6.2 | . . |
| $CH_4$ | 0.0 | 0.0 | 0.0 | 6.1 | . . |
| $C_2H_4$ | 0.0 | 0.1 | 0.2 | 2.0 | . . |
| $C_2H_6$ | 0.0 | 0.0 | 0.3 | 0.6 | . . |
| $C_3H_6$ | 0.1 | 0.2 | 0.3 | 7.3 | . . |
| $C_3H_8$ | 0.7 | 1.8 | 3.1 | 4.1 | 0.5 |
| Iso-$C_4H_8$ | 0.0 | 0.0 | 2.0 | 4.9 | 0.2 |
| *n*-$C_4H_8$ | 0.5 | 0.6 | | | |
| $C_4H_{10}$ | 98.3 | 96.5 | 92.2 | 68.8 | 99.3[b] |
| Liquid product | None | Trace | None | Trace | . . |
| C, % by wt. of charge | None | None | None | 0.5[a] | . . |

[a] CO not included.
[b] All iso-$C_4H_{10}$.

TABLE IV. CATALYTIC CRACKING OF PARAFFINS

| | *n*-Pentane | *n*-Heptane | | | Iso-octane | Parowax | |
|---|---|---|---|---|---|---|---|
| Experimental conditions | | | | | | | |
| Temperature, °C. | 500 | 500 | 550 | 600 | 500 | 500 | 500 |
| LHSV | 1.50 | 2.08 | 2.08 | 3.12 | 2.25 | 3.04 | 5.7 |
| Flow rate, moles/l./hr. | 13.0 | 14.2 | 14.2 | 20.9 | 13.6 | 6.8 | 13.7 |
| Gaseous product | | | | | | | |
| Moles/mole charge | 0.015 | 0.052 | 0.203 | 0.407 | 0.123 | 2.40 | 1.52 |
| Volume % | | | | | | | |
| $H_2$ | [a] | 4.5 | 6.5 | 5.1 | 5.9 | 6.1 | 6.8 |
| $CH_4$ | [a] | [a] | 4.3 | 6.9 | 15.3 | 4.9 | [a] |
| $C_2H_4$ | [a] | [a] | 8.3 | 21.0 | 1.2 | 2.3 | [a] |
| $C_2H_6$ | [a] | [a] | 6.5 | 12.6 | 0.7 | 2.2 | [a] |
| $C_3H_6$ | [a] | [a] | 25.8 | 28.0 | 8.2 | 30.5 | [a] |
| $C_3H_8$ | [a] | [a] | 14.2 | 6.3 | 1.9 | 7.3 | [a] |
| Iso-$C_4H_8$ | [a] | [a] | 6.4 | 5.5 | 17.3 | 11.9 | [a] |
| *n*-$C_4H_8$ | [a] | [a] | 10.6 | 8.5 | 13.3 | 18.4 | [a] |
| $C_4H_{10}$ | [a] | [a] | 17.4 | 6.1 | 36.2 | 16.4 | [a] |
| Total olefins | [a] | 45.1 | 51.1 | 63.0 | 40.0 | 63.1 | 67.2 |
| Total saturates | [a] | 50.4 | 42.4 | 31.9 | 54.1 | 30.8 | 26.0 |
| Material balance, wt. % of charge | | | | | | | |
| Gas | 1.2[b] | 2.5 | 8.5 | 15.0 | 4.9 | 30.2 | 21.5 |
| Liquid below original b.p. | None | 0.3 | 0.7 | 0.6 | 3.2 | 29.4[d] | 29.8[e] |
| Remaining product | 94.3 | 94.9 | 87.3 | 81.9 | 83.8 | 35.5 | 37.0 |
| Carbon | None | 0.1[c] | 0.1[c] | 0.2[c] | 8.1 | 1.7 | 11.7 |
| Loss | 4.5 | 2.2 | 3.4 | 2.3 | | 3.2 | |

[a] Not analyzed.
[b] Estimated from incomplete gas analysis.
[c] CO not included.
[d] To 145° C.
[e] To 250° C.

TABLE V. CATALYTIC AND THERMAL CRACKING OF DODECANES

| | *n*-Dodecane | | | Isododecane | | | |
|---|---|---|---|---|---|---|---|
| Catalyst | UOP-B | | None | UOP-B | | None | |
| Experimental conditions | | | | | | | |
| Temperature, ° C. | 500 | 550 | 550 | 500 | 550 | 500 | 550 |
| LHSV[a] | 3.3 | 3.2 | 0.27 | 3.04 | 3.1 | 0.21 | 0.30 |
| Flow rate, moles/l./hr.[a] | 14.5 | 14.1 | 1.18 | 13.2 | 13.6 | 0.94 | 1.31 |
| Gaseous product | | | | | | | |
| Moles/mole charge | 0.32 | 1.13 | 1.07 | 0.33 | 1.11 | 0.32 | 1.03 |
| Volume % | | | | | | | |
| $H_2$ | 6.5 | 27.1 | 7.4 | 7.9 | 15.7 | 11.1 | 9.6 |
| $CH_4$ | 8.8 | 7.1 | 17.9 | 20.9 | 20.8 | 24.1 | 32.4 |
| $C_2H_4$ | 5.1 | 6.0 | 26.9 | 2.2 | 2.0 | 1.1 | 2.1 |
| $C_2H_6$ | 3.2 | 2.9 | 15.0 | 1.2 | 0.6 | 1.9 | 1.6 |
| $C_3H_6$ | 25.8 | 23.8 | 16.5 | 18.9 | 22.4 | 6.2 | 9.2 |
| $C_3H_8$ | 13.7 | 8.2 | 5.7 | 3.1 | 2.2 | 2.7 | 2.7 |
| Iso-$C_4H_8$ | 8.7 | 7.0 | 1.7 | 16.1 | 14.9 | 39.3 | 28.3 |
| *n*-$C_4H_8$ | 10.4 | 10.2 | 7.9 | 15.3 | 13.0 | 2.1 | 6.4 |
| $C_4H_{10}$ | 17.8 | 7.7 | 1.0 | 14.4 | 8.4 | 11.5 | 7.7 |
| Material balance, wt. % of charge | | | | | | | |
| Gas | 8.0 | 21.2 | 19.2 | 7.7 | 23.0 | 7.2 | 21.6 |
| Liquid below original b.p. | 8.3 | 9.8 | 17.6 | 4.5 | 7.5 | 7.5 | 11.3 |
| Remaining liquid | 75.7 | 62.8 | 52.2 | 84.5 | 67.0 | 82.5 | 63.3 |
| Carbon | 8.0 | 1.9 | .... | 0.5[b] | 0.8 | .... | .... |
| Loss | | 4.3 | 11.0 | 2.8 | 1.7 | 2.8 | 3.8 |

[a] Based on 70 cc. free space in thermal runs and on 50 cc. catalyst in catalytic runs.
[b] CO not included.

cated only small amounts of $C_5$ and $C_6$ hydrocarbons. Compared with the run at 550° C., that at 600° C. gave a gas containing more $C_2$, less $C_4$, and more olefins. In spite of the large amount of $C_2$, the yield of $C_3$ and $C_4$ olefins was 47% by weight of the feed cracked, somewhat more than in the run at the lower temperature.

**Iso-octane (2,2,4-Trimethylpentane).** Iso-octane was cracked with the results shown in Table IV. Cracking was not extensive, but was two to three times more than that of *n*-heptane under the same conditions. The gas contained considerable quantities of methane, and large amounts of butenes and butanes. The *n*-butene formed indicates that isomerization occurred. Cracking to $C_4$ fragments was the principal reaction. The lower-boiling liquid distilled between 60° and 95° C., and there was no indication of $C_5$ hydrocarbons. The results are in contrast with those for *n*-octane reported by Egloff *et al.* (*3*), which showed little $C_4$ and much more $C_3$ and $C_5$. The extents of decomposition cannot be compared from the two sets of results, however, for the conditions differed considerably.

***n*-Dodecane.** Normal dodecane gave the results listed in Table V. In general, the reactions of this compound resemble those of cetane (discussed below). Gas was obtained in high yield and contained large amounts of $C_3$ and $C_4$ hydrocarbons, richer in olefins than in paraffins. The lower-boiling liquid contained much olefin, 80% in the 30–120° C. fraction from the run at 500° C. and about the same from the run at 550° C. The latter had 73.5% olefins in the $C_5$ cut and 78% in the $C_6$ cut. The 100–210° C. fraction from the run at 550° C. contained 32% aromatics, as well as 17% olefins. The tendency toward lower olefin and higher aromatic contents with increasing distillation temperature of the product is noteworthy. The distillation of the liquid product indicated that a wide variety of hydrocarbons from $C_5$ through $C_{10}$ was formed in the cracking of *n*-dodecane.

Results from thermal cracking of *n*-dodecane at 550° C. are also shown in Table V. The catalyzed decomposition is about ten times faster at this temperature, and the weight ratio of gas to cracked liquid product is also greater. The gas compositions differ considerably; the hydrogen content of the catalytic gas is somewhat high, which can be correlated with the relatively high carbon deposit; further, there is much less $C_1$ and $C_2$, more $C_3$ and $C_4$, a higher olefin/paraffin ratio, and more isomerization of butene. For equal amounts of total cracking, the yield of more valuable gas components (propylene, butenes, and butanes) in catalytic cracking is twice that in thermal cracking. The liquid fractions also differ considerably. The product from thermal cracking contained 100% olefins in the $C_5$ cut compared to 73.5% in the catalytic, and 83% olefins and no aromatics in the 100–210° C. fraction compared to 17 and 32%, respectively, in catalytic cracking.

**Isododecane.** This hydrocarbon (presumably chiefly 2,2,4,6,6-pentamethylheptane) from the hydrogenation of tri-isobutene from the cold acid polymerization process gave data collected in Table V. The cracking was rather limited, and the reactions were complex. On the whole, the behavior of isododecane is not unlike that of *n*-dodecane; the larger amounts of $CH_4$ and $C_4$ in the gas may be ascribed to the particular structure of isododecane. Analyses of liquid products showed the production of large amounts of olefins and even some aromatic material. The fraction 20–100° C. from the run at 500° C. contained 50% olefins. Fractions from the run at 550° C. had the following analysis: 20–50° C., 93% olefins; 50–100° C., 75% olefins; 100–175° C., 15% olefins, 14% aromatics; recovered isododecane, less than 1% olefins. Judged by boiling points, neopentane and neohexane were produced in small amounts.

Like *n*-dodecane, isododecane cracks about ten times as rapidly over the catalyst as it does thermally at 550° C. Comparison of catalytic and thermal products from isododecane shows that with a given amount of decomposition the catalyst gives a little less methane, much more propylene, much less isobutene, more *n*-butene, less total $C_4$ material, more total gaseous olefins, and less cracked liquid. The catalyst causes considerable production of *n*-butene, but the thermal reaction produces very little. When the more valuable gas components are totaled, the catalytic product is found to have an advantage of only about 10% by weight yield at 550° C. and even less at 500° C. Liquid products differed somewhat in the distribution of lower-boiling liquid and in analysis. The thermal fraction boiling from 100° to 175° C. contained 46.5% olefins and 11% aromatics, compared to 15% and 14%, respectively, in the corresponding catalytic fraction, both made at 550° C.

**Comparison of Normal and Isododecanes.** Catalytic cracking proceeds at a slightly higher rate with *n*-dodecane. Isododecane gives more methane and more butylene, and the ratios of gas to liquid are somewhat higher. The thermal results at 550° C. show similar rates of reaction for the normal and iso compounds,

TABLE VI. CATALYTIC AND THERMAL CRACKING OF CETANE

| | Catalytic Cracking | | | | | Thermal, This Work[a] |
|---|---|---|---|---|---|---|
| | This work | | | | (*3*) | |
| Experimental conditions | | | | | | |
| LHSV | 1.9 | 0.94 | 2.0 | 3.9 | 4.0 | 1.89 |
| Flow rate, moles/l./hr. | 6.5 | 3.2 | 6.7 | 13.2 | 13.5 | 6.45 |
| Temperature, ° C. | 450 | 500 | 500 | 500 | 500 | 500 |
| Process period, min. | 60 | 60 | 60 | 60 | 524 | 60 |
| Gaseous product | | | | | | |
| Moles/mole charge | 0.52 | 2.04 | 1.45 | 1.05 | 0.55 | 0.09 |
| Volume % | | | | | | |
| $H_2$ | 4.3 | 3.9 | .... | 2.7 | 1.5 | 6.2 |
| $CH_4$ | 1.8[b] | 5.1 | .... | 0.2 | 1.7 | 55.5[c] |
| $C_2H_4$ | 2.1 | 4.1 | .... | 2.2 | 1.0 | 38.6[d] |
| $C_2H_6$ | .... | 3.9 | .... | 1.9 | 2.0 | .... |
| $C_3H_6$ | 15.0 | 23.6 | .... | 29.0 | 32.8 | .... |
| $C_3H_8$ | 15.5 | 13.9 | .... | 12.9 | 12.6 | .... |
| Iso-$C_4H_8$ | 7.4 | 7.1 | .... | 10.6 | 11.5 | .... |
| *n*-$C_4H_8$ | 14.2 | 10.6 | .... | 17.5 | 21.0 | .... |
| $C_4H_{10}$ | 39.7 | 27.8 | .... | 23.0 | 16.0 | .... |
| Material balance, wt. % of charge | | | | | | |
| Gas | 11.4 | 40.7 | 28.6 | 22.2 | 11.1 | 1.6 |
| Gasoline to 200° C. | 13.5 | 25.6 | 21.4 | 17.6 | 6.9 | 2.2 |
| Above 200° C. | 74.8 | 32.9 | 48.7 | 56.4 | 81.6 | 95.8 |
| Carbon | 0.3[e] | 1.7[e] | 1.3 | 0.4[e] | .... | 0.2[e] |
| Loss | 0.0 | (−0.9) | 0.0 | 3.4 | 0.4 | 0.2 |

[a] 110-cc. Pyrex beads in reactor, but flow rates on a 50-cc. basis; comparable to run at 2.0 LHSV, but with Pyrex replacing catalyst.
[b] Including $C_2H_6$.
[c] Total saturates, carbon number 1.8.
[d] Total olefins, carbon number 2.4.
[e] CO not included.

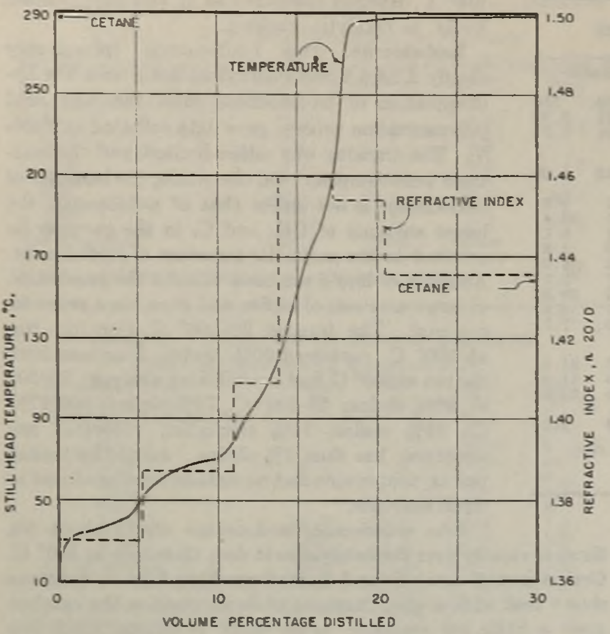


**Figure 1. Distillation Curve and Refractive Indices for Liquid Product from Cracking Cetane at 500° C. and 3.9 LHSV**

The 70% bottoms had a refractive index of 1.4358.

and a higher ratio of gas to liquid for isododecane. Isododecane forms more methane and $C_4$ material, the normal compound more $C_2$ and $C_3$ under these circumstances.

**Cetane (*n*-Hexadecane).** Cetane was cracked at 450° and 500° C. Thermal cracking (with Pyrex beads in the reactor) at 500° C. was found to be less than 5%; catalytic cracking at the same flow rate was 51.3%. The results are shown in Table VI, and for comparison the Universal Oil Products Company data (*5*) are included, though they were obtained with a somewhat different catalyst (silica-alumina-thoria).

The conditions covered are not extensive enough to fix the optimum gasoline yield and gas composition, but it is evident that lowering the temperature for a given flow rate increases the gasoline/gas ratio. The influence of temperature upon the composition of the gas does not appear to be pronounced except for the marked rise in olefin content with temperature.

The UOP work is not strictly comparable to ours because of the different conditions used, but qualitative agreement exists. Cracking was more complete in our experiments because of the shorter process periods. Analyses of fractions from a run at 500° C. and 2 LHSV showed the following:

| Fraction | Wt. % of Gasoline | Wt. % of Olefin | Analytical Method |
|---|---|---|---|
| $C_5$ | 45 | 54[a] | $H_2SO_4$ absorption |
| $C_6$ | 30 | 53.5 | Rosenmund Br No. |
| Above $C_6$ | 25 | .. | ... |

[a] 32% tertiary, 22% secondary.

The large percentages of branched olefin structures in the $C_4$ (Table VI) and $C_5$ cuts are of interest. Branched paraffins in the $C_5$ and $C_6$ cuts were indicated by distillation temperatures, as in the UOP work (*5*). Isobutane is prominent in the butanes. An analysis of a $C_4$ cut from cracking cetane at 500° C. and 1 LHSV showed iso-$C_4H_8$ = 18.9, *n*-$C_4H_8$ = 30.3, iso-$C_4H_{10}$ = 35.0, and *n*-$C_4H_{10}$ = 15.8%. The distillation curve above 80° C. for the run at 500° C. and 2 LHSV rose smoothly without plateaus, hence no specific compounds were identified. The small amounts of $C_7$, $C_8$, and higher hydrocarbons, compared to the large amount of $C_5$ and $C_6$ hydrocarbons which were found, is remarkable. $C_8$ hydrocarbons are not formed in important quantities (no more than 5% of the gasoline) and higher hydrocarbons are even less prominent. Results with cetane thus indicate that either $C_8$ and larger fragments are subsequently broken down, or only smaller molecules are formed in the first place.

Further analyses (Table VII) show that the olefin content of all fractions in the gasoline range is high under the conditions employed. About 10% aromatics are present in the $C_7$ and $C_8$ cuts, and 40 to 50% in the $C_9$-$C_{11}$ range, the latter constituting less than 15% of the total gasoline. The runs at the higher temperature gave products somewhat richer in both olefins and aromatics.

There was very little material boiling between 200° C. and the unchanged cetane (287° C.). Vacuum distillation of products from runs at 500° C. and 2 and 3.9 LHSV showed that this intermediate fraction was only 0.7% by weight of the charge.

Several experiments to find the effect of flow rate at 500° C. (Table VI) show that increasing the flow rate decreases the extent of cracking, increases the ratio of gasoline to gas, and increases the olefin content of the gas.

Figure 1 shows a distillation curve for liquid product from the run at 500° C. and 3.9 LHSV. The distillation was continued above 200° C. at 15 mm. pressure; the corrected boiling points are used in the figure. The distillation curve shows the same features of product distribution already mentioned for experiments at 2 LHSV. Aromatics are present in appreciable quantities in the $C_9$-$C_{11}$ range. The refractive indices from this and other distillations show that aromatic formation is favored by longer contact times. The product boiling above 200° C. consists of a small quantity of mixed aromatic and aliphatic hydrocarbons, together with much unchanged cetane.

**Parowax (Approximately *n*-$C_{24}H_{50}$).** To extend the series of *n*-paraffins into the range of higher paraffins, Parowax was used. Fractional crystallization of similar material and examination of the fractions showed the composition to be substantially normal paraffins (*9*). Melting points of the fractions indicated that the paraffins ranged from $C_{20}$ to $C_{28}$, with an average number of 23.8 carbon atoms.

Decomposition of Parowax at 500° C. (Table IV) was extensive. Products were similar to those from cetane, but had relatively less gas and more lower-boiling liquid. The lower-boiling liquid from Parowax, like that from cetane, contained much $C_5$ and $C_6$ material; in fact, this range made up 75% by weight of the liquid boiling below 145° C. in the run at 3.0 LHSV. The products from this run were even less saturated than those from cetane. The $C_5$ fraction contained 76% olefins, and the $C_6$, 73%. The gas was also rich in olefins. There was so little high-boiling gasoline in the product from the run at 3 LHSV that, when the stillhead temperature reached 145° C., further material could not be distilled at atmospheric pressure without some cracking. The remaining bottoms melted at 33-38° C. and therefore contained little besides unchanged Parowax. Product from the run at 5.7 LHSV was rapidly distilled to 250° C. with no apparent cracking,

Table VII. Hydrocarbon Group Analyses of Fractions from Catalytic Cracking of Cetane

(In Weight Per Cent)

| | 450° C., 2 LHSV | | | 500° C., 2 LHSV | | |
|---|---|---|---|---|---|---|
| Fraction[a] | Olefins | P + N[b] | Aromatics | Olefins | P + N[b] | Aromatics |
| $C_2$ | .. | .. | .. | 39 | 61 | .. |
| $C_3$ | 48 | 52 | .. | 57 | 43 | .. |
| $C_4$ | 34 | 66 | .. | 42 | 58 | .. |
| $C_5$ | 50 | 50 | .. | 58 | 42 | .. |
| $C_6$ | 45 | 55 | .. | 60 | 40 | .. |
| $C_7 + C_8$ | 24 | 64 | 12 | 58 | 34 | 8 |
| $C_9 + C_{10} + C_{11}$ | 36 | 26 | 38 | 30 | 15 | 55 |

[a] Corresponding to boiling ranges of paraffins, Cn.
[b] Paraffins + naphthenes.

and the fraction from 145° to 250° C. was about 5% by weight of the charge.

### CATALYTIC CRACKING

The results with the paraffins throw light on one of the important functions of the cracking catalyst, the acceleration of carbon-carbon bond rupture. It is evident that this is not a random acceleration, but that it is selective for certain bonds. Thus the first and second carbon-carbon bonds at the ends of *n*-paraffin chains are relatively inert to the action of the catalyst, for little methane or ethane is produced; the third carbon-carbon bond is rather easily broken, and those still farther toward the center of the molecule are even more so, although there is little preference among them. The tendency is to crack off only fragments with three or more carbon atoms. Following these primary ruptures, or simultaneously with them, further cracking of the larger fragments occurs. The products from *n*-hexadecane, for instance, consist largely of $C_3$ to $C_6$ hydrocarbons.

Our results and those in the references cited indicate that reactions other than cracking which the catalyst favors are: (*a*) production of aromatic compounds from normal paraffins; (*b*) isomerization, which seems to occur principally in olefins produced by cracking; and (*c*) hydrogen transfer. The aromatics are chiefly $C_8$ and higher. The reactions of olefin isomerization and saturation appear to be the most plausible explanation of the occurrence of branched aliphatics in the product, the isoparaffins resulting from saturation of the iso-olefins. No direct isomerization of paraffins has been observed in this work.

Comparison of catalytic cracking of normal and highly branched paraffins through the results obtained with *n*-heptane and iso-octane, and with *n*-dodecane and isododecane, show the rates of cracking of these compounds to be about the same for the same molecular weights. The branched compounds are of a particular type, having only methyl side chains and possessing quaternary carbon atoms. The gas analyses show decided differences. The branched compounds produce larger amounts of methane, less $C_3$, and more $C_4$ than do the corresponding normal compounds. The $C_4$ fractions from the branched compounds are relatively richer in olefins, especially isobutene. The production of more isobutene from these branched hydrocarbons is to be expected from their structure, and the greater amount of methane is viewed as a simple consequence of the numerical predominance of methyl groups. Although the differences in the products from the normal and iso compounds, in both thermal and catalytic reactions, can readily be traced to the molecular structures, it seems a little surprising that the rates of catalytic reaction are so nearly the same. Subsequent papers will show that analogous structural differences have a large effect in the case of aliphatic olefins and of alkyl aromatics, and more recent data on other isomeric paraffins show that structure has a considerable effect. Data on the effect of structure of paraffins (to be published later) will show that compensating influences are at work which account for the similar catalytic cracking rates of the pairs, *n*-heptane–iso-octane and *n*-dodecane–isododecane.

Figure 2 shows the effect of molecular size on rates of cracking of normal paraffins. The total percentage decomposed includes gas, liquid boiling below the original, and carbon. All results have been corrected to a no-loss basis. As the molecular weight increases, the amount decomposed catalytically under fixed conditions increases rapidly. The percentages of gas and of lower-boiling liquid from the *n*-paraffins are of interest. Below $C_8$ gas predominates, but above $C_8$ the relative amounts of gas and lower-boiling liquid are remarkably similar, except for Parowax where liquid is in excess. Gases from all normal paraffins are similar in composition, with very high contents of propylene, butenes, and butanes.

### COMPARISON WITH THERMAL CRACKING

Figure 2 also shows considerable acceleration of the cracking of normal paraffins by the catalyst, as indicated by the ratio of catalytic to thermal decomposition rates. The acceleration increases with molecular weight. For the thermal rates, average reaction velocity constants were used, based on a smoothed curve representing data in the literature (*2, 5, 8, 10, 13, 14*) and from the present work. Values taken for the first-order thermal velocity constants at 500° C. were (in $\text{sec.}^{-1}$): butane 0.00012, pentane 0.00022, heptane 0.0005, dodecane 0.0018, cetane 0.004, and Parowax 0.007; the last two values are less certain than the others. Catalytic reaction velocities were characterized by apparent constants computed from the first-order law:

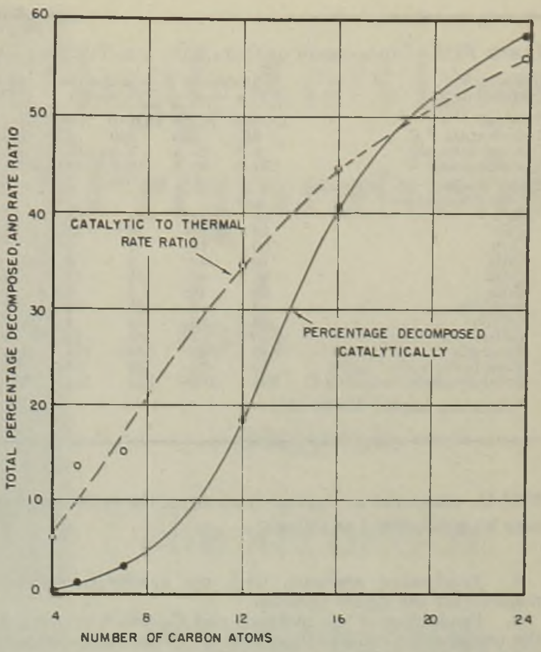


**Figure 2. Effect of Molecular Size on Catalytic Cracking of *n*-Paraffins and on Ratio of Catalytic to Thermal Cracking Rate at 500° C.**

Catalytic experiments at 13.7 moles per liter of catalyst per hour except butane at 8.3 moles.

$$k = (1/t) \ln [100/(100 - C)]$$

where $C$ = percentage cracked
$t$ = contact time, sec.

Values obtained were (in $\text{sec.}^{-1}$): butane 0.00073, pentane 0.0030, heptane 0.0076, dodecane 0.062, cetane 0.18, and Parowax 0.40. The catalytic rates have only qualitative significance, for although thermal cracking of normal paraffins obeys the first-order law fairly well, catalytic cracking does not; the apparent catalytic $k$ increases with space velocity. This causes the ratios of rates to depend somewhat on the space velocity employed in the catalytic experiments. Catalytic rates also depend on the process period to some extent. The ratios are therefore only viewed as giving an idea of the order of magnitude of the catalysis. It should also be noted that the contact time used for computing catalytic $k$ is based on the assumption of 100% void catalyst; actually the catalyst is only about 67% void. If the latter basis was used, the ratios would be 1.5 times those shown.

Thermal and catalytic reactions differ not only in rate, but also in nature. More explicitly, the catalyst selectively accelerates certain characteristically thermal reactions and induces some reactions not appreciable in thermal cracking. For these two reasons there are important differences in the results. The chief characteristics of catalytic cracking of normal paraffins at

Table VIII. Comparison of Catalytic and Thermal Cracking of Paraffins

| Hydrocarbon | *n*-Dodecane | | Isododecane | | Isododecane | | *n*-Octane | |
|---|---|---|---|---|---|---|---|---|
| Origin of data | This work | | This work | | This work | | (*3*) | (*10*) |
| Catalyst | UOP-B | None | UOP-B | None | UOP-B | None | UOP-B | None |
| Temperature, ° C. | 550 | 550 | 500 | 500 | 550 | 550 | 570 | 570 |
| Contact time, sec.[a] | 2.5 | 29.4 | 3.8 | 52.3 | 2.7 | 28.0 | 1.7 | 12.7 |
| % decomposed | 34.8 | 41.3 | 12.7 | 15.1 | 31.3 | 34.2 | 11.0 | 19.4 |
| Moles product per 100 moles feed decomposed | | | | | | | | |
| $H_2$ | 92 | 21 | 21 | 24 | 56 | 29 | 13 | 0.3 |
| $CH_4$ | 24 | 52 | 56 | 53 | 74 | 99 | 9 | 77 |
| $C_2H_4$ | 20 | 78 | 6 | 2.4 | 7 | 6.5 | 19 | 86 |
| $C_2H_6$ | 10 | 43 | 3 | 4.1 | 2 | 5 | 11 | 55 |
| $C_3H_6$ | 81 | 48 | 51 | 14 | 80 | 28 | 52 | 46 |
| $C_3H_8$ | 28 | 16 | 8 | 6 | 8 | 8 | 18 | 6.5 |
| Iso-$C_4H_8$ | 24 | 5 | 43 | 86 | 53 | 87 | 22 | 18 |
| *n*-$C_4H_8$ | 35 | 23 | 41 | 4.5 | 46 | 19.5 | | |
| $C_4H_{10}$ | 26 | 3 | 39 | 25 | 30 | 24 | 7 | 1.3 |
| Total gas | 340 | 289 | 268 | 219 | 356 | 306 | 151 | 290 |
| Total lower-boiling liquid | 53 | 71 | 53 | 76 | 41 | 54 | 89 | 36 |
| Total products, excluding C | 393 | 360 | 321 | 295 | 397 | 360 | 240 | 326 |

[a] Assuming catalyst 100% void.

500° C., compared to thermal cracking at the same temperature, may be summarized as follows:

1. Accelerated cracking, with the acceleration more pronounced for the higher paraffins.
2. Production of less methane and $C_2$, which is coupled with the tendency to crack to fragments of three or more carbon atoms. With large *n*-paraffins ($C_{16}$ and $C_{24}$) the catalysis operates to leave little cracked material above $C_{10}$, which is not the case thermally.
3. Greater formation of aromatics.
4. Formation of branched-chain aliphatics, whereas none appears thermally.
5. More extensive secondary reaction of the olefinic products, especially saturation, cracking, isomerization, and polymerization.

Evidence for item 1 is given in Figure 2. Item 2 is substantiated by gas analyses for *n*-octane and *n*-dodecane in Table VIII, and by data for cetane and Parowax outlined below, as well as by other less direct comparisons. Item 3 is shown by results with *n*-dodecane and cetane. Regarding item 4, formation of branched aliphatics has been noted in catalytic cracking of all normal paraffins above hexane, while only traces have been found in the products from thermal cracking under comparable conditions. Item 5 is introduced to explain the production of isobutane and the low olefin contents of higher-boiling fractions from catalytic cracking of normal paraffins. Data to support this item can be found in the publications from UOP laboratories (*1*, *3*, *15*), and more will be presented in later papers of this series.

Table VIII compares catalytic and thermal cracking results for *n*-octane and *n*- and isododecanes. Qualitative discussion of available evidence for *n*-dodecane and other compounds follows.

**Propane.** The thermal reactions have been carefully studied (*13*, *14*), but the catalytic work was too limited to permit detailed comparison. Roughly equal amounts of cracking and dehydrogenation occur in both cases.

**Butanes.** The thermal reactions are well known (*12*, *13*, *14*). The small amount of decomposition in the catalytic experiments makes comparison inexact. The ratio of dehydrogenation to other decompositions was roughly the same in thermal as cracking for both butanes.

***n*-Heptane.** Analyses of thermal products are not available.

**Iso-octane (2,2,4-Trimethylpentane).** Thermally (*2*) at 502° C. there was 11.4% decomposition with a contact time of 109 seconds, about one twentieth as fast a reaction as the catalytic. The gas analysis was like that from the thermal cracking of isododecane (Table V) and differed from the catalytic in showing less *n*-butene. Other differences cannot be stated with certainty.

***n*-Dodecane.** Thermal and catalytic results are presented in Tables V and VIII; the chief differences have already been pointed out. The thermal results agree well, in the gas analyses, with those of Dintses and Klabina (*2*), though the reaction velocity constant from their work is about three times that of ours.

**Cetane (*n*-Hexadecane).** Gault and coworkers studied the vapor-phase thermal cracking (*4*). Although the data obtained are limited, they can be used for several comparisons. The gas produced thermally at 500–575° C. had the following analysis: $H_2$ none, $CH_4$ 23%, $C_2H_4$ 32%, higher olefins 28%, higher saturates 17%. The much lower methane and ethylene contents in the catalytic gas are evident from Table VI. The lower-boiling liquids in both cases contained large amounts of olefins and some aromatics but were not so predominantly made up of $C_5$ and $C_6$ material in the case of the thermal reaction. For the same temperature of cracking, the higher-boiling gasoline fractions from the thermal treatment contained considerably less aromatics. There is a tendency for cracking to take place at the end of the chain in pyrolytic treatment, especially at higher temperatures, but this is not observed to the same extent catalytically.

**Paraffin Wax.** This material is composed almost entirely of normal paraffins. Heymans (*7*) concluded that the thermal cracking of Rangoon paraffin wax at 10 to 30 mm. pressure and 450° to 700° C. occurred largely at the ends of the chains, in contrast to catalytic behavior. Data on the vapor phase cracking of paraffin waxes were also given by van Peski (*11*) from experiments at 545° C. and about 2.7 atmospheres pressure in the presence of steam, which may be compared to our catalytic results with Parowax. The thermal cracking led to a regular series of aliphatic fractions, from $C_6$ through at least $C_{15}$, and the fractions were about 90% *n*-olefin throughout. Catalytic cracking yielded relatively little material above $C_8$ (except uncracked wax), the higher fractions had very low olefin contents, and the lower fractions contained considerable amounts of branched olefins and paraffins.

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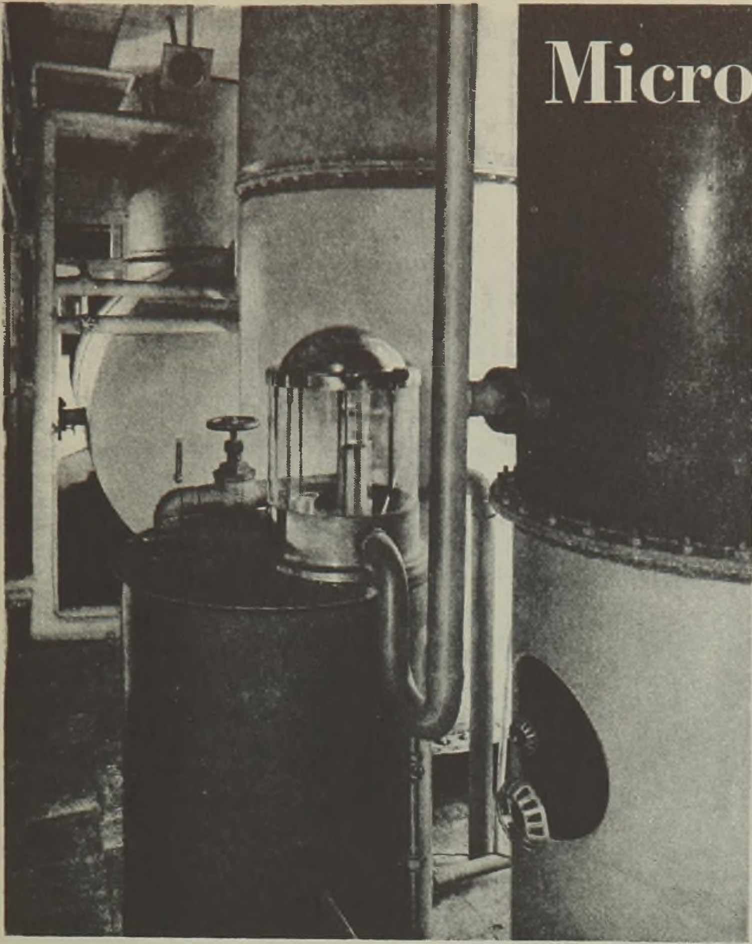


# Microbial Amylase Preparations

## CONVERSION AGENTS FOR ALCOHOLIC FERMENTATION

**LU CHENG HAO**
**AND**
**JOHN A. JUMP**
***Joseph E. Seagram & Sons, Inc.***
***Louisville, Ky.***

**Alcohol Recovery Still**

THE use of amylases as saccharifying agents in brewing and fermentation is an old art, the beginnings of which are lost in antiquity. Takamine (*6*) first introduced mold bran, produced by growing *Aspergillus oryzae* on wheat bran, to the modern distillery, but its use did not find favor on account of the slight off-flavor of the alcohol resulting from the use of mold. During recent years mold amylase preparations as saccharifying agents in industrial alcohol fermentation of corn have been studied by Underkofler, Fulmer, and associates (*2*, *3*, *8*). Underkofler (*7*) discussed briefly the relative merit of microbial amylases and malt, and drew the conclusion that "when malt and mold bran are used under optimum conditions for each, the alcohol yields obtained are essentially the same, based on total dry matter going into the process, with apparently a slight advantage for the mold-bran".

In previous studies most of the mold amylase preparations tested were prepared in the laboratory. These materials have proved to be efficient conversion agents. However, they are not available in quantities for large scale experiment. A number of mold and bacterial amylase preparations are on the market, but information is limited concerning the use of these preparations in the alcoholic fermentation of grain. It should be of interest to determine the relative efficiency of these materials as liquefying and saccharifying agents in alcoholic fermentation, because these determinations will show whether any of the commercially available amylase preparations can be utilized with advantage as

**The activity of a number of commercial bacterial and mold amylase preparations as conversion agents in alcoholic fermentation were determined. Three samples of bacterial amylase preparations were used to replace malt in premalting corn mash. Successful liquefaction was obtained in all cases. A number of mold amylase preparations in crude, extract, and precipitated forms were used in the saccharification of starch in corn mash. The weights of mold amylase preparations and that of malt required to produce equally satisfactory alcohol yields from the same weight of corn have the following ratios:**

**Malt: crude mold amylase preparations = 8:5**
**Malt: extract of mold amylase = 8:4 to 8:6**
**Malt: precipitated mold amylase = 8:0.4 to 8:1.2**

**The alcohol yields obtained from the mold amylase preparations range from 89 to 94% of the theoretical yield, calculated on the basis of starch in corn. From these yields it can be concluded that nearly all of the commercial mold amylase preparations tested are good conversion agents in alcoholic fermentation. However, their use on a commercial scale is dependent on their respective costs.**

TABLE I. SOURCES OF MICROBIAL AMYLASE PREPARATIONS

| Name of Sample | Producer |
|---|---|
| Bacterial amylase I | [a] |
| Bacterial amylase II | Wallerstein Co., Inc. |
| Bacterial amylase III | [a] |
| Mold bran I | Frederick Stearns & Co. |
| Mold bran II | Wallerstein Co., Inc. |
| RHozyme | Rohm & Haas Co., Inc. |
| Maltase No. 20 | |
| RHozyme Intermediate | |
| Maltase Intermediate | |
| Converzyme No. 503 | Joseph E. Seagram & Sons, Inc. (lab. preparation) |
| Converzyme No. 505 | |
| Converzyme No. 511 | [a] |
| Polidase-C | Schwarz Lab., Inc. |
| Polidase-S | |
| Diatane type 1211 | Jeffrey Lab. |
| Diatane B-10 | |
| Taka-Diastase | Parke, Davis & Co. |
| Alase | Takamine Lab. |
| Crystazyme | Frederick Stearns & Co. |

[a] Name of producer not revealed because of limited supply of product or other technicalities.

sources of amylase (Table I). In addition, it is hoped that the data presented here will clarify the long-existing controversy between the merit of malt and that of mold amylase preparations as conversion agents.

### FERMENTATION PROCEDURE

In general, the fermentative determination of the activity of microbial amylase preparations as conversion agents of grain mash was conducted in the same way as that designated for malt conversion by Stark, Adams, Scalf, and Kolachov (*5*) with the exception that the conversion temperature was 130° F. when mold amylase preparations were used. (The conversion temperature for malt was 145° F.) The beer was distilled after 64 hours of fermentation. The specific gravity of the distillate was determined with the immersion reflectometer at 17.5° C. (63.5° F.). Comparison of the results of "per cent alcohol" in distillate determined with the reflectometer and those determined with a pycnometer showed that there was no appreciable difference between the two methods, and that the reflectomer is a reliable instrument for determining the percentage of alcohol in distillate obtained from fermentations with mold amylase preparations as conversion agents. The yeast culture used a strain of *Saccharomyces cerevisiae* labeled "DCL" at this laboratory. All fermentations were run in triplicate.

The quantities of microbial amylase preparation for liquefaction and for saccharification are estimated, on the basis of the potency of each, by a method employed at this laboratory (*4*). The liquefying power is determined on the basis of the degradation of soluble starch into dextrins, and the saccharifying power is determined on the basis of the production of reducing sugar from soluble starch using Fehling solution as a testing agent.

The quantities of each amylase preparation are so chosen that they will give liquefying and saccharifying activities equivalent to those of one part and eight parts distillers' malt, respectively. If the quantity of amylase preparation thus estimated fails to give satisfactory activity, a higher concentration is generally employed to determine whether the same activity can be maintained with less amylase preparation.

The efficiency of the microbial amylase preparations is expressed as: conversion efficiency, alcohol yield in terms of proof gallons per bushel of corn, and alcohol yield in terms of proof gallons per bushel of total grain. These expressions are interpreted and calculated as follows:

CONVERSION EFFICIENCY. This term expresses the efficiency of conversion of starch in corn by the conversion agent. It is calculated on the basis of alcohol obtained from corn alone. The quantities of alcohol produced from yeast inoculum, premalt, and conversion agent are deducted from the total amount of alcohol. This net amount of alcohol produced from corn alone divided by that theoretically obtainable from corn gives the conversion efficiency. The theoretical yield is calculated on the basis of starch determined by the A.O.A.C. diastase-hydrochloric acid method (*1*). A detailed sample calculation was given in a previous publication (*2*).

YIELD BASED ON CORN. The alcohol yield in proof gallons per bushel of corn is calculated from the grams of absolute alcohol obtained from each fermenter containing 56.3 grams of corn. The factor for converting grams of absolute alcohol from 56.3 grams of corn to proof gallons of alcohol per 56 pounds of corn is:

$$\left(\frac{56}{56.3} \div 6.60\right) \times 2 = 0.301$$

where 6.6 = weight of 1 gal. of absolute alcohol, lb.

The yield of run 361 was therefore:

$$18.02 \times 0.301 = 5.42 \text{ proof gal./bu. (wet basis)}$$

$$5.42 \times \frac{100}{100 - 10.4} = 6.04 \text{ proof gal./bu. (dry basis)}$$

YIELD BASED ON TOTAL GRAIN. A previous publication (*5*) gives the derivation of factors and equations involved. The alcohol yield in proof gallons per bushel of total grain is calculated as follows:

$$\text{P.G./bu.} = [(\% \text{ by vol. of alcohol as read in 100 cc. of dist.}) - (\text{initial sugar concn. of yeast mash per 100 ml.} \times 0.0208)] \times \frac{100 \text{ (ml. of dist.)}}{175 \text{ (ml. of mash distd.)}} \times \text{concn. of mash (gal. of mash/bu.)} \times \frac{2}{100}$$

According to the above example, the yield of run 361 was:

$$\text{P.G./bu.} = [12.01 - (14 \times 0.0208)] \times \frac{100}{175} \times 38 \times \frac{2}{100} = 5.08 \text{ (wet basis)}$$

The composite moisture of the total grain was 10.16%, therefore:

$$\text{P.G./bu.} = 5.08 \times \frac{100}{(100 - 10.16)} = 5.66 \text{ (dry basis)}$$

It is evident that, when calculations are based on alcohol from corn alone, the alcohol produced from the premalt and conversion agent is disregarded. The "conversion efficiency" and "yield in

TABLE II. COMPARISON OF ALCOHOL YIELDS FROM CORN MASH LIQUEFIED WITH BACTERIAL AMYLASE PREPARATIONS

| Run No. | Liquefying Material | Weight Ratio: Liquefying material | Weight Ratio: Converzyme No. 505 | Weight Ratio: Corn[a] | Conversion Efficiency, % | Yield[b], P.G./Bu. Based on: Corn | Yield[b], P.G./Bu. Based on: Total grain |
|---|---|---|---|---|---|---|---|
| 361 | Malt (control)[c] | 1.0 | 8 | 91 | 91.4 | 6.03 | 5.66 |
| 362 | Bacterial amylase I | 1.0 | 8 | 91 | 91.5 | 6.04 | 5.72 |
| 363 | Same | 1.5 | 8 | 91 | 92.9 | 6.14 | 5.77 |
| 342 | Same | 1.0 | 5 | 91 | 91.0 | 6.02 | 5.79 |
| 343 | Same | 0.5 | 5 | 91 | 86.8 | 5.72 | 5.53 |
| 432 | Bacterial amylase II | 1.0 | 8 | 91 | 93.7 | 6.18 | 6.00 |
| 433 | Same | 1.5 | 8 | 91 | 93.5 | 6.17 | 5.99 |
| 442 | Bacterial amylase III | 1.0 | 8 | 91 | 92.9 | 6.14 | 5.78 |
| 443 | Same | 0.5 | 8 | 91 | 91.5 | 6.04 | 5.70 |
| 360 | Concd. HCl | 3.0[d] | 8 | 91 | 95.5 | 6.30 | 6.10 |
| 393 | Same | 3.0 | 8 (malt) | 91 | 84.0 | 5.54 | 5.44 |

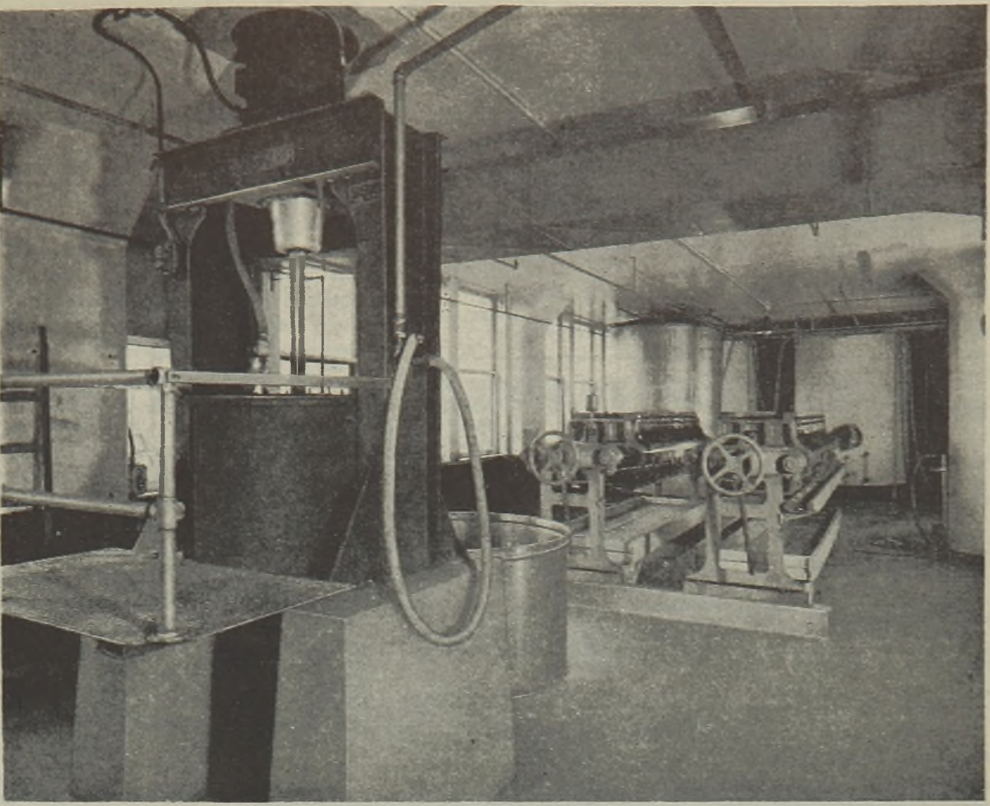
[a] Weight of corn in the mash is the same in all the fermentation runs; this corn has a starch content of 61.8% and a moisture content of 10.4%.

[b] All yields are calculated on a dry basis.

[c] This malt has a starch content of 50.0% and a moisture content of 8%.

[d] The acidity of the mash during cooking is approximately 0.06 *N*. The pH is adjusted to 5.6 before the addition of conversion material.

proof gallons per bushel of corn" are, therefore, of interest only for comparison of the activity of the different amylase preparations as conversion agents. On the other hand, the "yield in proof gallons per bushel of total grain" is an index for comparing the total alcohol production of the process as a whole, including the amount of alcohol derived from the different conversion materials used, and is of practical interest.



Centrifuge and Shriber Pressure Filters

#### BACTERIAL PREPARATIONS AS LIQUEFYING AGENTS

It is well known that bacterial amylase preparations produced from *Bacillus subtilis* or *Bacillus mesentericus* have high liquefying action on starch, and these enzyme preparations are characterized by maximum activity in neutral and alkaline solutions and at high temperature. Bacterial amylases have not found utilization in distillery practice because they produce very little sugar but large amounts of dextrin.

It was thought that bacterial amylase preparations might be used for thinning cooked mash—in other words, to replace premalt. Two samples in extract form (bacterial amylase preparations I and II, Table I) and one in purified powdered form (bacterial amylase preparation III) were tested. The alcohol yields from corn mash liquefied with these preparations and subsequently saccharified with Converzyme No. 505 (Table I) are summarized in Table II.

These results indicate that, when equal weights were used, bacterial amylase preparations gave either equal or slightly higher alcohol yields than did malt. With the exception of bacterial amylase III, a concentrated preparation, when the weight of bacterial amylase preparation was reduced to half that of malt, there was a considerable drop in alcohol yield. Although there was no significant increase in alcohol yield when bacterial amylase preparation was used, the mash liquefied with bacterial amylase had a considerably lower viscosity than that liquefied with an equal amount of malt. When tested with a 10-ml. pipet, the ratios of time of flow of 10 ml. of each mash through the pipet were:

$$\text{Water}: \left\{\begin{array}{l}\text{Bacterial-}\\\text{amylase-}\\\text{liquefied}\\\text{mash}\end{array}\right\} : \left\{\begin{array}{l}\text{Malt-}\\\text{liquefied}\\\text{mash}\end{array}\right\} = 3:15:100$$

Therefore, as far as liquefaction of starch is concerned, these bacterial amylase preparations are probably several times as potent as malt. However, as far as alcoholic fermentation is concerned, with the exception of bacterial amylase III, a weight of bacterial amylase preparation equal to that of malt is required to produce satisfactory alcohol yield.

Run 360 (Table II) indicates that acid is still the most efficient liquefying agent for the pretreatment of grain mash. Theoretical yields of 93–95% were consistently obtained with 5% of crude mold amylase preparations. However, in our experience acid was satisfactory only when mold amylase preparation was the saccharifying agent. When malt is used, acid cooking is detrimental to the alcohol yield (run 393, Table II). Possibly acid hydrolyzes starch to dextrins, a fraction of which can be saccharified by the amylases in mold amylase preparations although it is not attacked by the amylases in malt.

#### MOLD PREPARATIONS AS CONVERSION AGENTS

The activities of sixteen samples of mold amylase preparations as conversion agents in the alcoholic fermentation of corn mash were determined. These samples include eight crude preparations in the form of mold bran, two intermediate preparations which are the water extract of the mold bran, and six precipitated and purified preparations in powdered form. These samples are commercial products except the Converzymes, which were prepared in the laboratory by growing *Aspergillus oryzae* on wheat bran by the aluminum pot method (*2*). The processes employed in producing the commercial samples were not revealed by the producers. Data on the alcohol yields from corn mash converted with crude mold amylase preparations are given in Table III.

These data indicate that all of the crude amylase preparations gave satisfactory conversion efficiencies. Among the samples tested at two concentration levels, there is no significant difference between 5 or 8 parts of amylase preparation employed. Generally speaking, any of the preparations tested gave higher conversion efficiency and higher alcohol yield based on corn than those obtained by using malt. The alcohol yields, in proof gallons per bushel of total grain, obtained from mold amylase preparation were approximately the same as those obtained from malt.

TABLE III. COMPARISON OF ALCOHOL YIELDS FROM CORN MASH CONVERTED WITH CRUDE MOLD AMYLASE PREPARATIONS

| Run No. | Conversion Material: Name | Conversion Material: Wt. ratio[a] | Conversion Efficiency, % | Yield, P.G./Bu., Based on: Corn | Yield, P.G./Bu., Based on: Total Grain |
|---|---|---|---|---|---|
| 611 | Malt (control) | 8 | 89.0 | 5.87 | 5.74 |
| 301 | Converzyme No. 603 | 8 | 90.0 | 5.93 | 5.58 |
| 361 | Converzyme No. 505 | 8 | 91.4 | 6.03 | 5.66 |
| 302 | Mold bran I | 8 | 89.5 | 5.89 | 5.56 |
| 322 | Mold bran I | 5 | 90.0 | 5.93 | 5.73 |
| 482 | Mold bran II | 8 | 91.0 | 6.00 | 5.63 |
| 483 | Mold bran II | 5 | 90.8 | 5.98 | 5.76 |
| 702 | Diatane T-1211 | 5 | 90.0 | 5.93 | 5.74 |
| 602 | Polidase-C | 8 | 91.9 | 6.06 | 5.72 |
| 703 | Converzyme No. 511 | 8 | 93.0 | 6.15 | 5.90 |

[a] The weight ratio of the other two components of the mash composition was 91 parts corn and 1 part liquefying material (malt) in each case.

TABLE IV. COMPARISON OF ALCOHOL YIELDS FROM CORN MASH CONVERTED WITH INTERMEDIATE MOLD AMYLASE PREPARATIONS

| Run No. | Conversion Material: Name | Conversion Material: Wt. ratio[a] | Conversion Efficiency, % | Yield, P.G./Bu., Based on: Corn | Yield, P.G./Bu., Based on: Total grain[b] |
|---|---|---|---|---|---|
| 581 | Malt (control) | 8 | 88.6 | 5.85 | 5.73 |
| 582 | RHozyme Intermediate | 4 | 93.6 | 6.17 | 5.96 |
| 583 | RHozyme Intermediate | 4 | 94.0 | 6.20 | 5.99 |
| 561 | Malt | 8 | 89.0 | 5.87 | 5.74 |
| 562 | Maltase Intermediate | 6 | 93.5 | 6.17 | 5.88 |
| 563 | Maltase Intermediate | 12 | 94.6 | 6.25 | 5.67 |

[a] Other components of mash composition: 91 parts corn and 1 part liquefying material (malt) in each case.

[b] These intermediate mold amylase preparations are in liquid form. However, in calculating total grain yield, the intermediate mold amylase preparations are considered as parts of the total grain bill.

The malt used for control fermentations was the same quality as that used in the Seagram plant during 1943. The malt used in run 611 has a Lintner value of 175°, which is inferior to the quality of prewar malt. The conversion efficiency (89.0%) is approximately 1 to 2% lower than that generally obtainable from prewar malt using water control (without stillage) fermentation.

Two samples of intermediate mold amylase preparations, RHozyme Intermediate and Maltase Intermediate, were used as conversion agents. These intermediate preparations are extracts of crude preparations and are in liquid form. The alcohol yields obtained from corn mash, converted with these intermediate mold amylase preparations, are summarized in Table IV.

These data show that RHozyme and Maltase Intermediate preparations are excellent conversion agents. The mashes converted with these preparations were considerably thinner than those converted with malt or any crude amylase preparation. With four parts of RHozyme Intermediate or six parts of Maltase Intermediate preparations, conversion efficiencies and alcohol yields (based on total grain) were considerably higher than those with eight parts of malt.

Samples of six purified amylase preparations were tested for their efficiency as conversion agents. All of these preparations are in powdered form. The alcohol yields from corn mash converted with these purified mold amylase preparations are compared in Table V[1].

These data show that nearly all of the samples tested were preparations of high amylase concentration. As little as 0.25 or 0.375 part gave higher conversion efficiencies and alcohol yields than did the malt control. However, in this limited number of determinations, the respective quantities of the different samples tested may not be the optimum concentrations. The authors were more interested to know the minimum quantity of each amylase preparation which will give an activity comparable to that of eight parts of malt, because the quantity of fungal amylase required would have a definite bearing upon the application from an economic viewpoint.

### MIXTURES OF MALT AND MOLD AMYLASE PREPARATION

Mixtures containing one part malt and five parts crude mold amylase preparation were used as saccharifying agents in addition to the one part of malt used for premalting. Diatane T-1211 and Diatane B-10 were chosen for these experiments. Alcohol yields obtained from corn mash converted with these mixtures and those obtained from the Diatane control (without the extra one part of malt) are compared in Table VI.

These results indicate that the addition of one part of malt to five parts of Diatane increased considerably the conversion efficiency. Although the Diatane preparations were the only samples used in this connection, evidence from other fermentation studies showed that other amylase preparations have the same effect. Run 733 indicated that one part of malt used for conversion and one part used for premalting could be eliminated when three parts of concentrated hydrochloric acid were utilized in cooking the mash. The acidity of the mash during cooking was approximately 0.06 *N*. The mash cooked with acid had a low viscosity, and the time for completing the fermentation was shorter than that of a normal fermentation using premalt. The disadvantage of using acid cooking is that the mash must be neutralized before the addition of the conversion agent, which will be an added manipulation in plant practice as well as added cost.

### EFFECT OF PARTIAL ADDITION ON ALCOHOL YIELD

It has been reported (*2*) that, when mold amylase preparation is added at intervals, the alcohol yield can be improved. Approximately three fifths of the total amylase preparation is added at the time of conversion, and the balance is put into the fermenter after 20 hours of fermentation. Alcohol yields obtained

TABLE V. COMPARISON OF ALCOHOL YIELDS FROM CORN MASH CONVERTED WITH PURIFIED MOLD AMYLASE PREPARATIONS

| Run No. | Conversion Material: Name | Conversion Material: Wt. ratio[a] | Conversion Efficiency, % | Yield, P.G./Bu., Based on: Corn | Yield, P.G./Bu., Based on: Total grain |
|---|---|---|---|---|---|
| 231 | Malt (control) | 8.0 | 88.0 | 5.87 | 5.66 |
| 252 | RHozyme | 0.375 | 89.1 | 5.88 | 5.87 |
| 233 | RHozyme | 0.25 | 88.0 | 5.81 | 5.80 |
| 232 | Maltase No. 20 | 0.275 | 91.0 | 6.00 | 5.98 |
| 552 | Taka-Diastase | 1.50 | 89.4 | 5.90 | 5.88 |
| 603 | Polidase-S | 0.375 | 90.4 | 5.96 | 5.95 |
| 542 | Alase | 1.15 | 91.3 | 6.04 | 5.98 |
| 543 | Alase | 1.90 | 92.5 | 6.11 | 6.06 |
| 742 | Crystazyme | 0.375 | 93.0 | 6.15 | 6.14 |

[a] Amounts used were estimated on the basis of potency of these materials, determined according to an unpublished method. for determining amyloclastic and saccharogenic powers used at Seagram laboratories. Other components of mash composition: 91 parts corn and 1 part liquefying material (malt) in each case.

TABLE VI. COMPARISON OF ALCOHOL YIELDS FROM CORN-MASH-CONVERTED PREPARATIONS AND 1% MALT

| Run No. | Conversion Material | Mash Compn., Wt. Ratio[a]: Conversion material | Mash Compn., Wt. Ratio[a]: Liquefying material (malt) | Conversion Efficiency, % | Yield, P.G./Bu., Based on: Corn | Yield, P.G./Bu., Based on: Total grain |
|---|---|---|---|---|---|---|
| 631 | Malt | 8 | 1 | 88.6 | 5.86 | 5.73 |
| 702 | Diatane T-1211 (control) | 5 | 1 | 90.0 | 5.93 | 5.74 |
| 731 | Diatane T-1211<br>Malt | 5<br>1 | 1 | 94.0 | 6.20 | 5.94 |
| 741 | Diatane B-10<br>Malt | 5<br>1 | 1 | 94.6 | 6.24 | 5.98 |
| 733 | Diatane B-10 | 5 | 3[b] | 96.5 | 6.37 | 6.15 |

[a] 91 parts corn in each case.

[b] Concentrated hydrochloric acid.

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[1] Because some of the samples of mold as well as bacterial amylase preparations used in this investigation are intended for other uses (for instance, Taka-Diastase is designated as a digestant of starch foods), the data presented here do not justify any conclusion drawn on the relative merits of these samples as liquefying or saccharifying agents outside of those in the alcoholic fermentation of grain under specified conditions. The authors hope they did not discredit any of the samples.

from corn mash cooked with acid and subsequently converted with Converzyme No. 505, with and without the partial addition method, are compared in Table VII. These results confirm that there is an increase of 1 to 2% in conversion efficiency as well as in alcohol yield when the mold amylase preparation is added at intervals.

TABLE VII. EFFECT OF PARTIAL ADDITION OF MOLD AMYLASE PREPARATION ON ALCOHOL YIELD

| Run No. | Wt. Ratio of Converzyme No. 505[a] |  | Conversion Efficiency, % | Yield, P.G./Bu., Based on: |  |
|---|---|---|---|---|---|
|  | 1st addition | 2nd addition |  | Corn | Total grain |
| 412 | 8 | .. | 94.0 | 6.20 | 5.88 |
| 413 | 5 | 3 | 96.2 | 6.35 | 6.10 |
| 402 | 5 | .. | 96.0 | 6.27 | 6.05 |
| 403 | 3 | 2 | 96.2 | 6.35 | 6.10 |

[a] The mash composition contained 91 parts by weight of corn in each case.

## SUMMARY AND CONCLUSIONS

1. The three bacterial amylase preparations tested gave satisfactory liquefaction of cooked mash when a weight of bacterial amylase equal to that of the malt (or half that of malt in case of the concentrated bacterial amylase preparation) was used.

2. All of the crude mold amylase preparations studied were efficient conversion agents. When mold amylase preparations were used, the conversion efficiency was higher than that obtained with malt. The alcohol yields, in proof gallons per bushel of total grain, resulting from crude mold amylase preparation and those from malt are generally the same.

3. Nearly all the intermediate and purified mold amylase preparations tested were excellent conversion agents. The concentration of the different preparations required to give satisfactory conversion efficiency varied from 0.25 to 1.5 parts in the case of the purified preparations, and from four to six parts in the case of the intermediate preparations.

4. A mixture of one part malt and five parts Diatane T-1211 or Diatane B-10 gave considerable increase in conversion efficiency as well as in alcohol yield. Yields of alcohol over 5.9 proof gallons per bushel of total grain (dry basis) were successfully obtained. [The Diatane preparations were the only samples tried for the mixed amylase (malt-mold) effect on this investigation.]

5. Cooking the mash with three parts of concentrated hydrochloric acid seemed to be the most efficient method for liquefying mash. Conversion efficiencies as high as 96.5 and alcohol yields of 6.15 proof gallons per bushel of total grain were obtained with acid cooking and Diatane.

6. Slight improvement of alcohol yield of 1 to 2% by the addition of mold amylase at intervals was confirmed.

7. From the study of these sixteen samples of crude, intermediate, and purified mold amylase preparations, it can be concluded that nearly all of the commercial mold amylase preparations tested are good conversion agents in alcoholic fermentation. However, their use on a commercial scale depends on their cost. Any of the mold amylase preparations studied in this investigation can be used if it is available at a price proportionally comparable to that of malt.

## ACKNOWLEDGMENT

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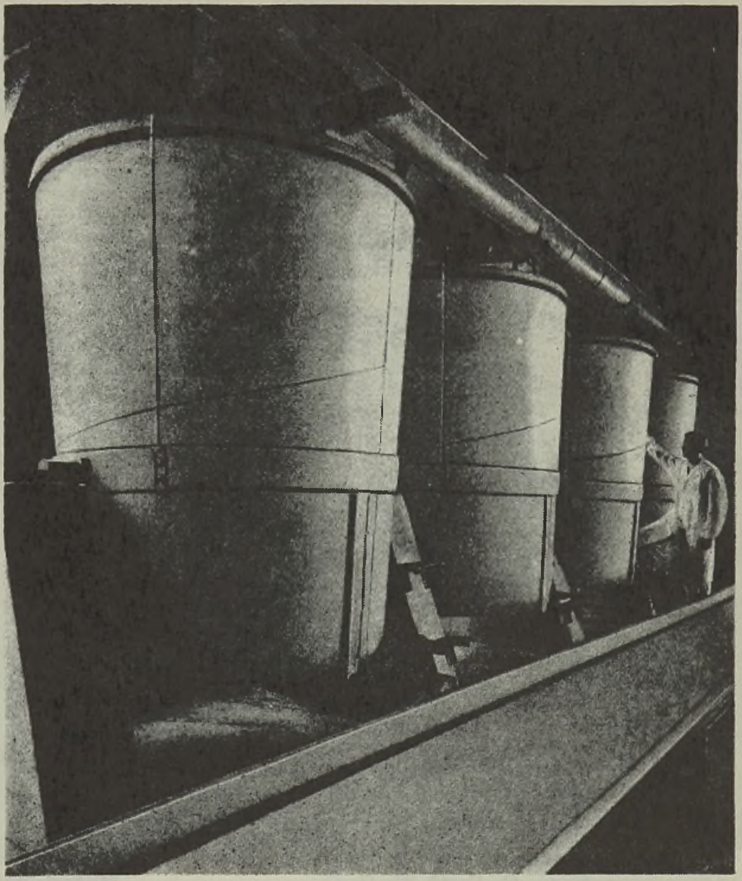


**Countercurrent Extraction Percolators**

# POLYTHENE

## Physical and Chemical Properties

**FREDERICK C. HAHN, MAURICE L. MACHT,
AND DAVID A. FLETCHER**

*E. I. du Pont de Nemours & Company, Inc., Arlington, N. J.*

**The hydrocarbon resin, polythene, recently became available commercially from domestic sources. The low electrical losses, along with high resistance to moisture and chemicals and toughness over a wide range of temperatures, have led to wide usage, particularly in the electrical field; these properties indicate other potential applications. The unusual resistance of this material to various chemicals suggests other fields for its use; data show the effects of exposure to various chemicals on the physical properties. They point to such applications as special types of equipment—containers, gaskets, tubing, etc. As a means of protecting metal surfaces from corrosion and applying polythene coatings in general, the process of flame spraying the powdered material is described. Certain flame-sprayed compositions show good adhesion to metals and give excellent protection against corrosion by water, brine, etc. Data are presented on other physical properties of polythene, such as the relation of density or volume to temperature.**

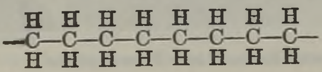
NUMEROUS polymers of ethylene have been prepared by many investigators by direct polymerization (*15*). These experiments yielded liquid hydrocarbons of relatively short chain lengths. Early workers synthesized small amounts of solid hydrocarbons of greater chain length by various chemical means, such as the decomposition of diazomethane (*2*), action of sodium on decamethylene bromide (*4*), and other reactions; but even these products were also of relatively low molecular weight. Subsequently Fawcett and Gibson started their historic fundamental studies of the effect of high pressure on chemical reactions, including polymerization (*10*). As a result of these researches Fawcett, Gibson, and Perrin (*9*) were the first to find that it was possible to obtain solid polymers of ethylene of sufficiently large molecular weight to be attractive for use in plastics.

"Polythene" is a generic name originated by Imperial Chemical Industries and adopted by du Pont to define those polymers of ethylene suitable for use in plastics. The solid or semisolid polymers included under this generic name may be further described as the substantially saturated chain hydrocarbons of which the average individual molecules are formed from about 100 or more ethylene units. The term "polythene" includes, therefore, a series of polymers of ethylene of various average molecular weights.

The present paper is concerned chiefly with polythene of the type and grade developed especially for electrical uses and having an average molecular weight in the neighborhood of 18,000 to 20,000. This product, like others in the higher ranges of molecular weight or viscosity, is tough and flexible over a wide range of temperatures (including very low ones), is translucent, and is normally white in color. Its structure results in unusual water resistance and characteristic electrical properties, such as extremely low power factor and low dielectric constant, along with high resistivity and high dielectric strength. The unusual combination of electrical and mechanical properties makes polythene suitable for the insulation of high-frequency and high-voltage equipment. The resistance of this material to water and chemical attack marks it as outstanding for waterproofing, corrosionproofing, gasketing in chemical plants, containers, and sheeting for packaging (*19*, *20*, *21*).

### STRUCTURE

CHEMICAL. Polythene is composed of long chains of methylene groups, which in the simplest way may be represented structurally as follows:



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Its molecular structure, as disclosed by x-ray studies, was thoroughly investigated by Bunn (*3*). The principal crystalline constituent of polythene represents the simplest type of crystalline structure in hydrocarbons. Bunn's data show the unit cell to be orthorhombic, containing four $CH_2$ groups, with a fiber-identity period of 2.53 Å. and an average distance between chains of 4.30 Å. This corresponds to planar zigzag carbon chains, with atoms separated by the usual 1.54 Å., and the tetrahedron valence angle of ordinary normal paraffins, as found by Hengstenberg (*13*) and others. Its spatial arrangement is best illustrated by the Hirschfelder model (Figure 1).

PHYSICAL. Polythene is essentially a microcrystalline plastic containing some amorphous material of similar composition, and its mechanical behavior resembles in many respects that of nylon. The arrangement of its microcrystalline components, or crystallites, may vary considerably according to the source and treatment of the sample. In polythene which has not had any special pretreatment, the crystallites tend to occur in a structure of spherulitic type, which on x-ray examination gives an over-all effect of random distribution of crystallites. It consists largely of spherulites which are radial or tangential aggregates of crystallites having, under ideal conditions, a gross structure of spherical shape. Microscopic evidence suggests the radial internal structure rather than the tangential, although this conclusion is not fully supported by the behavior in polarized light. The spherulitic structure is best seen under the polarizing microscope (Figure 2*A*).

The size of the spherulites can be varied by thermal treatment. By shock cooling, for example, a sheet can be made to contain only a few spherulites large enough to be resolved by the ordinary microscope. Such sheets are more transparent and flexible than ones which have been slowly cooled. In slowly cooled films the spherulites may measure 20 microns or more.

If tension is applied to a test specimen of sheeting at ordinary temperature, the elongation during the first phase of the stretching, up to about 100%, is substantially reversible, and if tension is released during this phase, the specimen recovers to a large extent instantly and then in a short time almost completely. When the

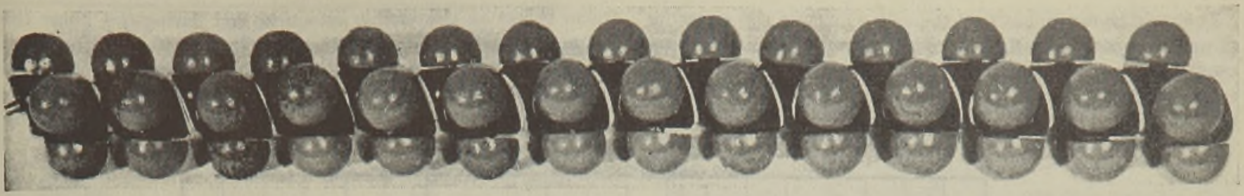

Figure 1. Hirschfelder Spatial Model of Polythene

tensile stress exceeds a certain critical value, a second phase of stretching occurs, up to about 600–750%, in which a permanent orientation of the crystallites takes place and the specimen necks down as cold drawing proceeds.

Cold drawing effects a change in appearance of the gross structure which may be seen by comparison of Figure 2*A* with 2*B*. The surface of the unstretched film shows a roughness under the microscope, and there are numerous valleys between the spherulites. In Figure 2*B* the valleys have been elongated. It would appear that, when the film is stretched, the material in the spherulites is drawn out into a different arrangement.

The rearrangement of the crystallites and long molecules in the amorphous portion, into position parallel to the direction of drawing, can be detected by measurement of birefringence (Figure 2*C*) or by x-ray examination.

Orientation may be effected also by cold rolling a sheet, and the extent of such orientation may be varied by the conditions of the rolling operation. This general phenomenon of orientation is of great interest, both scientifically and commercially.

### INFLUENCE OF MICROCRYSTALLINE STRUCTURE ON PHYSICAL PROPERTIES

The microcrystallinity of polythene appears to be an important factor in the changes in certain of its physical properties with temperature, for the reason that the microcrystalline condition itself is strongly influenced by temperature. As the material is heated from room temperature, it reaches a definite range of temperature within which there is a transition from crystalline to amorphous condition. As this temperature range is approached, the rate of change of certain physical properties with temperature becomes greater. This phenomenon is illustrated by curves showing the variations of refractive index, density, coefficient of expansion, and specific heat with temperature. Figure 3 shows the change of index of refraction with temperature; the change in this property in the vicinity of 80–100° C. appears to be caused by the disappearance of a certain crystalline phase as the result of fusion or solution. Double refraction disappears in this temperature range; however, under the polarizing microscope there is some evidence of persistence of crystalline structure up to about 112° C. Above 110–115° C. the relation of refractive index to temperature is a straight line, typical of polymers of liquidlike structure such as natural rubber and polyisobutylene. Analogous phenomena are illustrated by the curves showing variations of density (*14*), thermal coefficient of cubical expansion, and specific heat (*14*) with temperature (Figure 4). The high values for specific heat of polythene just below the melting point may be attributed to either heat of fusion or heat of solution—that is, fusion if the liquid phase has the same composition as the solid, or solution if the two phases are not identical.

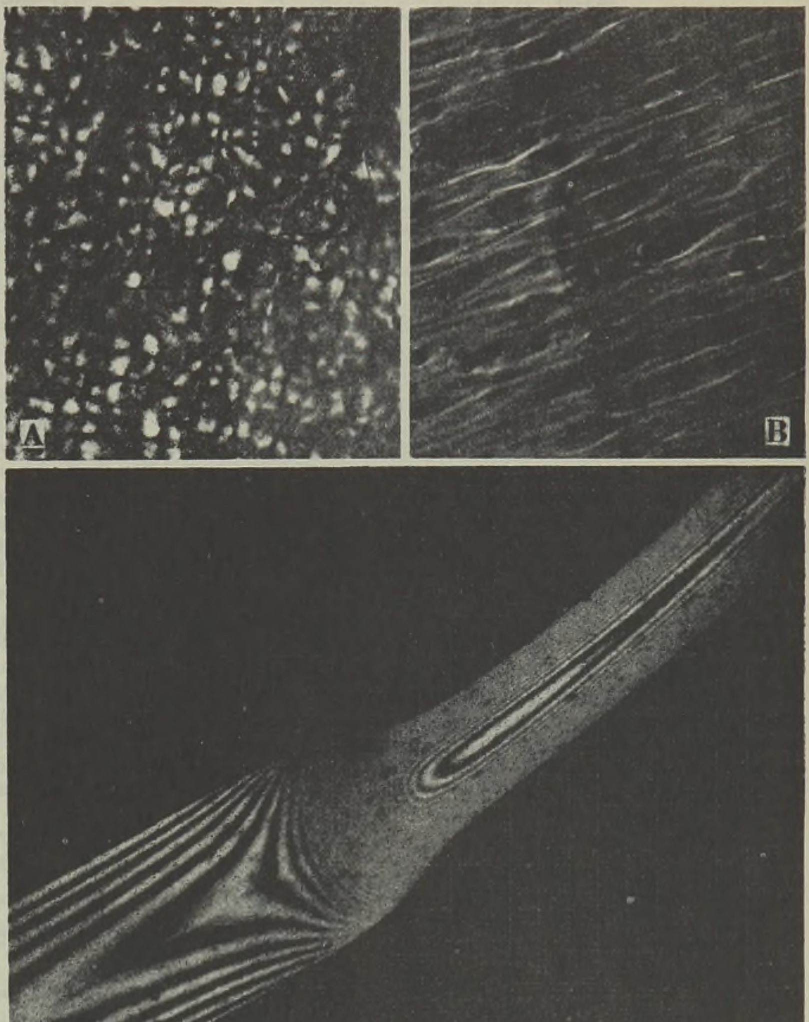

Figure 2. Photomicrographs (× 1000) of Polythene under Polarized Light

*A.* Undrawn, showing spherulites *B.* Drawn, showing spherulites *C.* Drawn filament

It should be mentioned that the values given in this paper for physical properties are typical of polythene but will not apply exactly to every specimen, since the properties are subject to some variation according to the source or type of the polythene, and the method of making the test specimen.

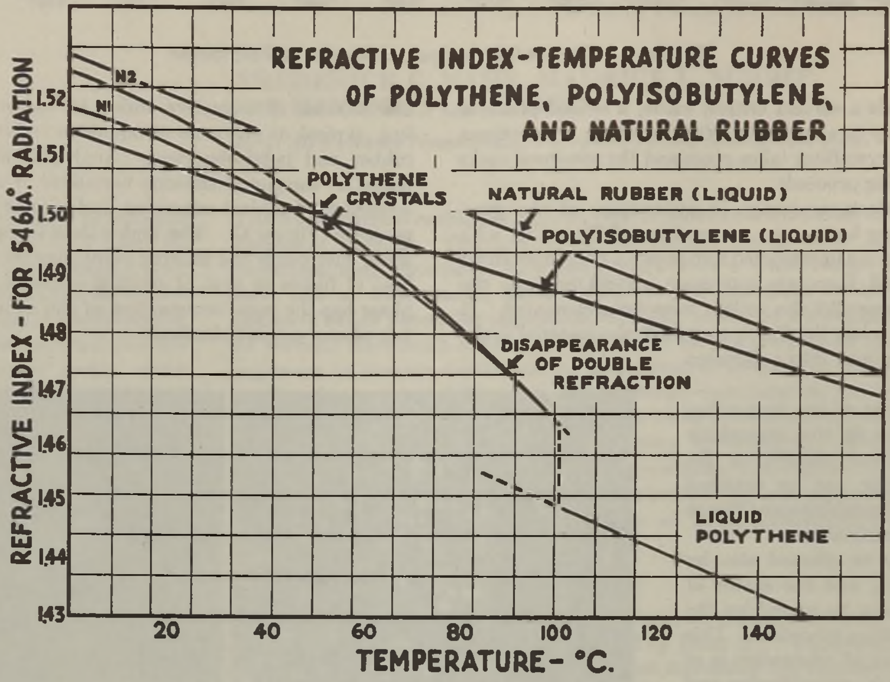

Figure 3. Effect of Temperature on Refractive Indices of Polythene, Polyisobutylene, and Natural Rubber

### PROPERTIES

MECHANICAL. Comparison with other plastics shows that polythene combines a number of good mechanical properties. As Figure 5 shows, the stiffness of polythene places it in a category between those materials known as rigid plastics and those termed nonrigid plastics. The stiffness of polythene, in common with that of other well known plastics, varies considerably with temperature.

Table I reports mechanical properties of polythene at 77° F. In the cases of some properties in which temperature is of particular importance, variations with temperature will be shown later.

The stress-strain diagram of Figure 6 shows that the application of tension to the test specimen causes elongation in a regular manner over the entire length until the stress has reached a critical value. Beyond this point the further application of tension effects an irreversible extension, and during this phase the elongation proceeds under nearly constant stress until the specimen has been cold-drawn to the ultimate extent over its whole length. Further application of tension results in a further elongation and then in failure. The elongation produced by cold drawing is of the order of 600–750% in sheeting and of the order of 50% in injection-molded specimens. Its magnitude depends upon the nature of the polythene, the conditions under which the specimen has been prepared, and the conditions under which the drawing is done (e.g., the rate of stretching). The ease with which cold drawing is effected is dependent upon a number of factors such as average molecular weight, distribution of molecular weight, method of fabrication of specimen, and temperature. The tensile strength is, of course, much greater when calculated per unit of cross section of drawn material than when calculated per unit of cross section of undrawn material.

The tensile strength of polythene, calculated on the original undrawn cross section, varies from about 800 pounds per square inch at 70° C. to about 5000 at −60° C. (Figure 7).

THERMAL. Table II presents the thermal characteristics of polythene. The low flow temperature indicates the ease with which this material can be extruded and molded. The heat-

TABLE I. MECHANICAL PROPERTIES OF POLYTHENE AT 77° F.

| Property | Value | A.S.T.M. Method of Test |
|---|---|---|
| Tensile strength, lb./sq. in. | 1900 | D6384–2T[a] |
| Elongation, % | 50[b]; 600–750[c] | D638–42T[e] |
| Modulus of elasticity, lb./sq. in. | 14,600 | D638–42T |
| Flexural strength, lb./sq. in. | 1,700 | D650–41T |
| Stiffness, lb./sq. in. | 13,300 | D747–43T |
| Impact strength (Izod), ft.-lb./in. | [d] | ....... |
| Rockwell hardness | R27 | D229–43 |
| Tear resistance, lb./in. of thickness | 440[e] | D624–41T |
| Shear strength, lb./sq. in. | 990[f] | [g] |

[a] For thin sheets, tested by method D412, die C: tensile, 1700–2400 lb./sq. in.; elongation, 200–600%.
[b] Injection-molded specimen, 0.25 inch thick.
[c] Sheeting.
[d] Did not break in a 4 ft.-lb. machine.
[e] Specimen 0.075 inch thick.
[f] Specimen 0.040 inch thick.
[g] Johnson shear jig.

TABLE II. THERMAL CHARACTERISTICS OF POLYTHENE

| Property | Value | Method of Test |
|---|---|---|
| Flow temp., ° C. | 104 | D569-43 |
| Deformation under load, % at 122° F./158° F. % | 0.6–0.8 | [a] |
| Strain-release temp., ° F. | 165–180 | M–15[b] |
| Yield temp., ° F. | 140 | M–8[b] |
| Heat-distortion temp., low-load, ° F. | 122 | [c] |
| Coefficient of linear expansion per ° F. (range 77–122° F.) | $25 \times 10^{-5}$ | D696–42T |
| Coefficient of cubical expansion per ° F. | (Fig. 4B) | ....... |
| Thermal conductivity, B.t.u./hr./sq. ft./°F./in. | 2.4 | [d] |
| Brittleness temp., ° C. | Below −50 | D746–43T |
| Specific heat | (Fig. 4C) | ...... |

[a] Proposed addition to A.S.T.M. D621–41T.
[b] Designation of method developed in authors' laboratory.
[c] Proposed revised method of A.S.T.M. D648, 66 lb./sq. in.
[d] Cenco-Fitch apparatus.

TABLE III. ELECTRICAL PROPERTIES OF POLYTHENE

| Property | Value | A.S.T.M. Method of Test |
|---|---|---|
| Dielectric strength, short-time, volts/min. | 475 (0.125 in.) | D149–40T |
| Volume resistivity, ohm-cm. | $10^{15}$ | D257–38 |
| Dielectric constant | | |
| 60 cycles | 2.3 | D150–42T |
| $10^3$ cycles | 2.3 | D150–42T |
| $10^6$ cycles | 2.3 | D150–42T |
| $10^8$ cycles | 2.3 | ....... |
| Power factor | | |
| 60 cycles | <0.0005 | D150–42T |
| $10^3$ cycles | <0.0005 | D150–42T |
| $10^6$ cycles | <0.0005 | D150–42T |
| $10^8$ cycles | <0.0005 | ....... |

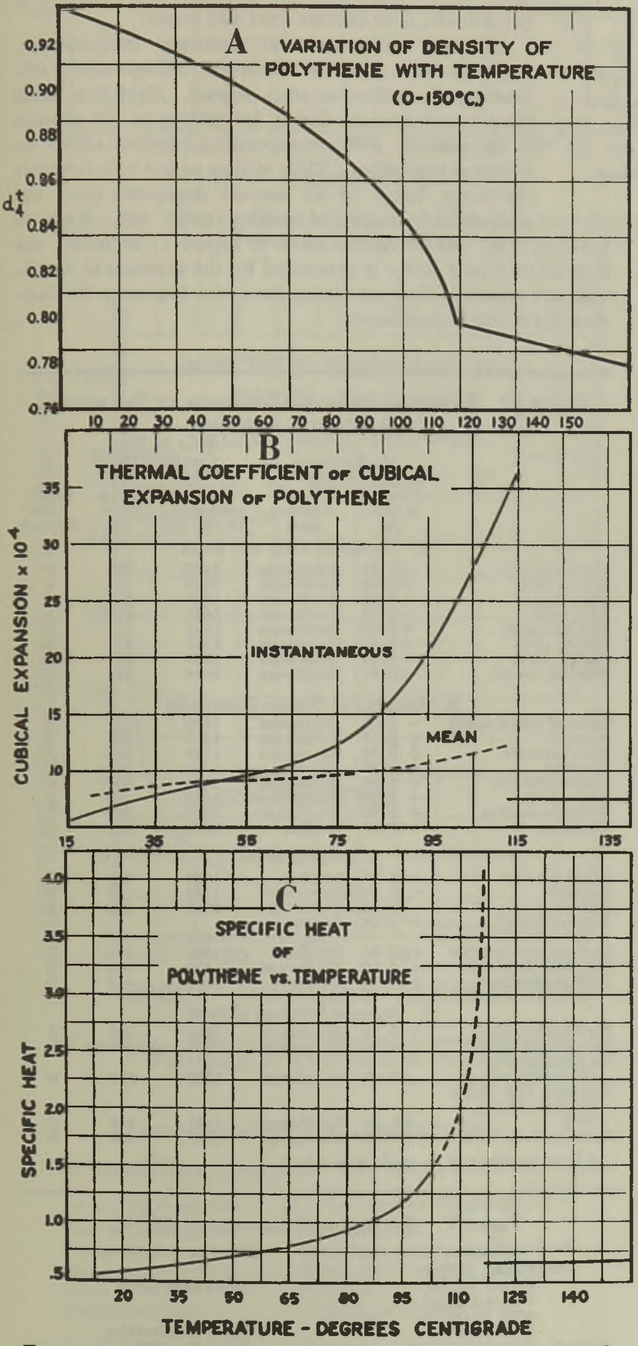

**Figure 4. Effect of Temperature on Density, Thermal Coefficient of Cubical Expansion, and Specific Heat of Polythene**

distortion temperature is indicative of ability to withstand normal service temperatures under low load, and the low value for deformation under load is exceptionally good for a plastic which is not rigid. The toughness of polythene at low temperatures is unusual for a material of its stiffness. In A.S.T.M. Test D746–43T the brittleness temperature of polythene is consistently below −50° C.

ELECTRICAL. It is in the field of electrical properties that polythene is most outstanding (*5*). Table III reveals the combination of properties which, in conjunction with its mechanical properties, chemical resistance, water resistance, and ease of working, has accounted for its acceptance in the field of electrical insulation, particularly for high-frequency systems.

The dielectric constant and power factor remain constant over a wide range of frequencies, and the dielectric constant changes little over the temperature range −50° to 220° F. (Figure 8). Figure 9 shows the variation of the dielectric strength of compression-molded polythene with thickness. Since polythene has very low moisture absorption (0.01 by A.S.T.M. method D570–42), its electrical properties are practically unaffected by changes in humidity or by immersion in water.

BEHAVIOR TOWARD WATER, SOLVENTS, AND CHEMICALS. The rate of transfer of water vapor by polythene is extremely low and is lower in thick sheets than in thin. Figure 10 shows the relation of permeability to thickness of cast sheeting and of sheeting made by compression molding. Permeability was measured by the method of Church and Scroggie (*4A*).

Not only is polythene resistant to water vapor, but total contact of one side of the film with liquid water has no effect on rate of transfer. It is not readily wetted by water; for example, it has a contact angle of 90° advancing or 70° receding, measured on a clean surface.

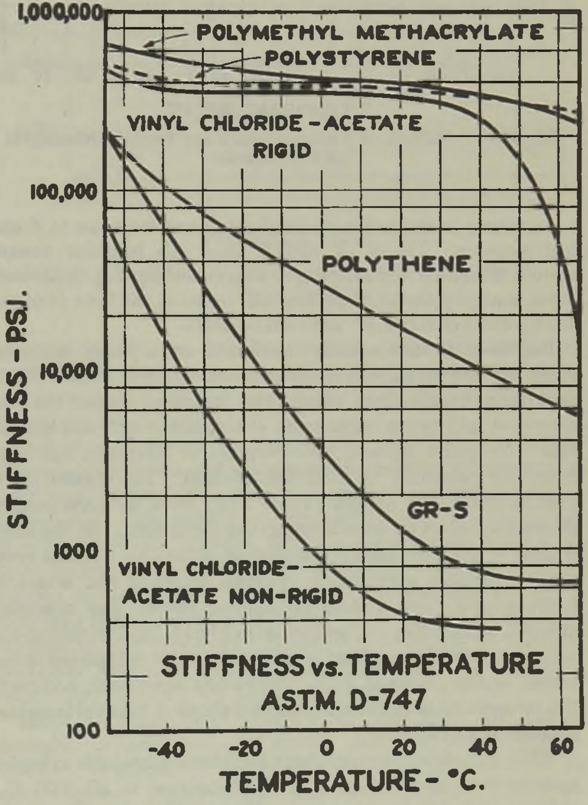

**Figure 5. Effect of Temperature on Stiffness of Polythene and Other Substances**

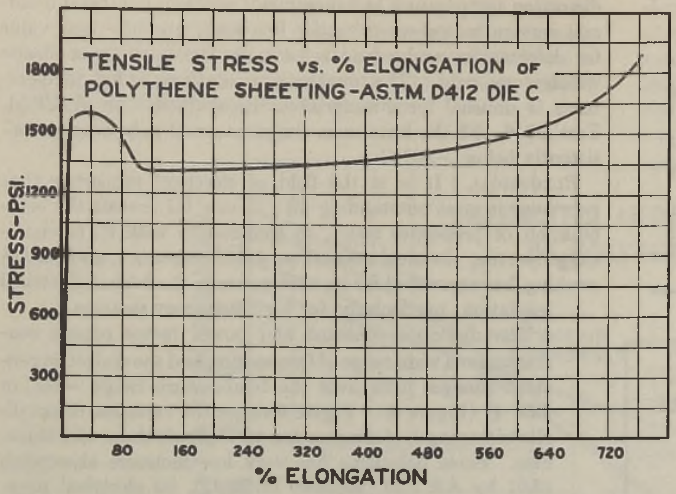

Figure 6. Typical Stress-Strain Data for Polythene Sheeting as Determined by A.S.T.M. Method D412, Die C

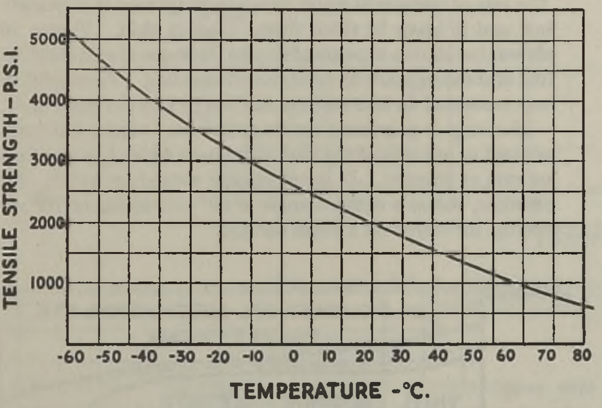

Figure 7. Effect of Temperature on Tensile Strength of Polythene

Polythene is unusual in its insolubility and inertness to chemical reagents. Tables IV and V show the behavior toward certain chemicals and solvents of polythene sheeting, 0.020 inch thick, made by the block process and tested in the form of pieces cut by die C of A.S.T.M. test method D412.

Polythene is substantially unaffected, at ordinary temperatures, by concentrated hydrochloric and sulfuric acids. Nitric acid has no visible effect, although on prolonged contact the concentrated acid causes impairment of tensile strength and elongation. No active solvent, either organic or inorganic, has been found for polythene at room temperature. The organic compounds containing oxygen (Table IV*B*) have no permanently destructive effect on tensile strength or elongation. Of the compounds of this class tested, camphor oil is the only one that even swells polythene appreciably. Certain aliphatic and aromatic hydrocarbons have a more pronounced effect. For example, gasoline, lubricating oil, carbon tetrachloride, and trichlorobenzene show definite swelling action; the latter compound is retained to the extent of 26%. Judged by hand tests, however, the strength of the material immediately after removal from the reagents is still good.

While at ordinary temperatures polythene is insoluble in liquid hydrocarbons and halogenated hydrocarbons at 80-100° C., these solvents dissolve it readily and completely. The extremely rapid increase in the solubility of standard grade polythene within this temperature range is probably due to the change in the proportion of material from the microcrystalline to the liquidlike state, which also appears to occur in this temperature range.

Polythene is substantially unaffected by solutions of a variety of salts (Table IV*D*).

No comprehensive study has been made of chemical resistance at elevated temperatures. Table V shows the effect of a few materials under such conditions (*14*).

Solutions of polythene in organic solvents gel on cooling, and the gels then slowly begin to show syneresis. When first formed, the gels are crumbly and may easily be disintegrated into fine particles, but as they lose solvent, they become hard and horny.

Although quite inert at ordinary temperatures, polythene is subject to oxidation, halogenation, sulfonation, and nitration when heated. Oxidation takes place to some extent during hot milling in the absence of antioxidant, with corresponding injurious effects on electrical properties. Thus, milling on hot rolls increases the power factor by an amount dependent upon the temperature, length of milling time, and clearance between rolls. As the dotted curve of Figure 11 indicates, the increase in power factor is prevented by the presence of a suitable antioxidant. Such an antioxidant also improves the outdoor durability of polythene.

Table IV. Effect of Various Chemicals on Polythene after 3-Month Contact

| | On Removal from Reagent | | After 24 Hrs. Conditioning at Room Temp. | | |
|---|---|---|---|---|---|
| | Change in wt., % | Appearance | Tensile strength, lb./sq. in. | Elongation, % | Resistance Rating[a] |
| | *A.* Inorganic Acids and Bases | | | | |
| $H_2SO_4$, concd. | +0.13 | No change | 1458 | 462 | E |
| $H_2SO_4$, 10% | +0.04 | No change | 1370 | 483 | E |
| HCl, concd. | +0.13 | No change | 1406 | 258 | G |
| HCl, 10% | +0.20 | No change | 1442 | 336 | E |
| $HNO_3$, concd. | +3.02 | No change | 1093 | 71 | F |
| $HNO_3$, 10% | +0.22 | No change | 1387 | 325 | E |
| NaOH, 50% | +0.13 | No change | 1432 | 313 | E |
| $NH_4OH$, concd. | +0.31 | No change | 1378 | 371 | E |
| | *B.* Oxygenated Organic Compounds | | | | |
| Ethanol (denatured) | − 0.02 | No change | 1550 | 421 | E |
| Acetone | + 0.03 | No change | 1363 | 379 | E |
| Ethyl acetate | + 2.76 | No change | 1295 | 325 | E |
| Dioxane | + 0.38 | No change | 1368 | 382 | E |
| Butyraldehyde | + 3.06 | No change | 1245 | 417 | E |
| Linseed oil | + 0.88 | No change | 1410 | 483 | E |
| Triethanolamine | + 0.08 | No change | 1408 | 379 | E |
| Camphor oil | +17.42 | Swollen | 1375 | 483 | G |
| | *C.* Hydrocarbons | | | | |
| Ethyl gasoline | +11.75 | Swollen | 1430 | 508 | G |
| Benzene | − 0.86 | No change | 1464 | 429 | E |
| Xylene | − 0.70 | No change | 1623 | 479 | E |
| Lubricating oil | + 7.54 | Swollen slightly | 954 | 167 | F |
| Carbon tetrachloride | +22.35 | Swollen | 1560 | 475 | E |
| Ethylene dichloride | + 0.80 | No change | 1526 | 300 | E |
| Trichlorobenzene | +26.33 | Swollen | 1450 | 442 | G |
| | *D.* Aqueous Solutions of Salts | | | | |
| Na bisulfite, 10% | 0.17 | No change | 1310 | 483 | E |
| Ca chloride, 15% | 0.70 | No change | 1380 | 483 | E |
| Ca hypochlorite (bleaching soln.) | +0.06 | No change | 1330 | 375 | E |
| Duponol ME (fatty alcohol sulfate), 10% | +0.04 | No change | 1225 | 463 | G |
| Ferric sulfate, 15% | +0.02 | No change | 1307 | 467 | E |

[a] E = excellent, G = good, F = fair.

Table V. Effect of Reagents at 100° C.

| Reagent | Effect on Polythene |
|---|---|
| Concd. HCl | None after 24 hr. |
| Dilute $HNO_3$ | |
| Dilute $H_2SO_4$ | |
| 50% NaOH | |
| Concd. $HNO_3$ | Some discoloration |
| Concd. $H_2SO_4$ | Some charring |

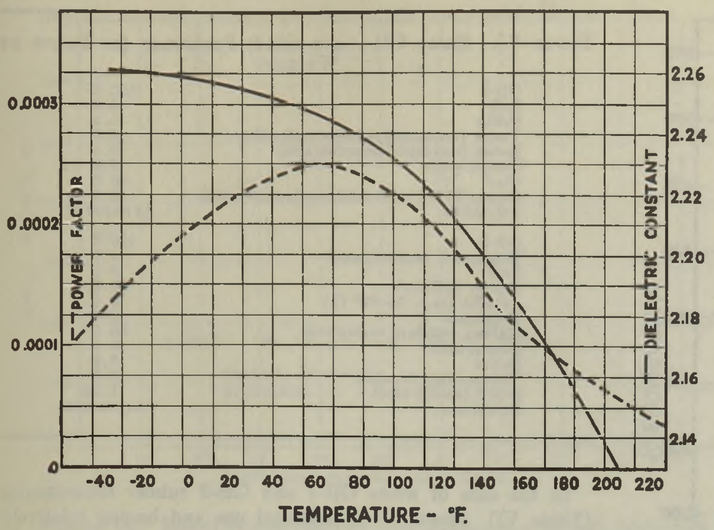

Figure 8. Effect of Temperature on Dielectric Constant and Power Factor of Polythene

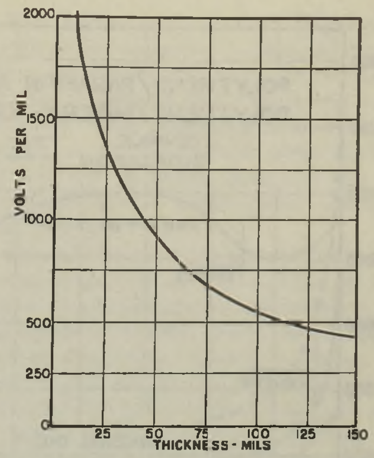

Figure 9. Relation of Dielectric Strength of Polythene to Thickness

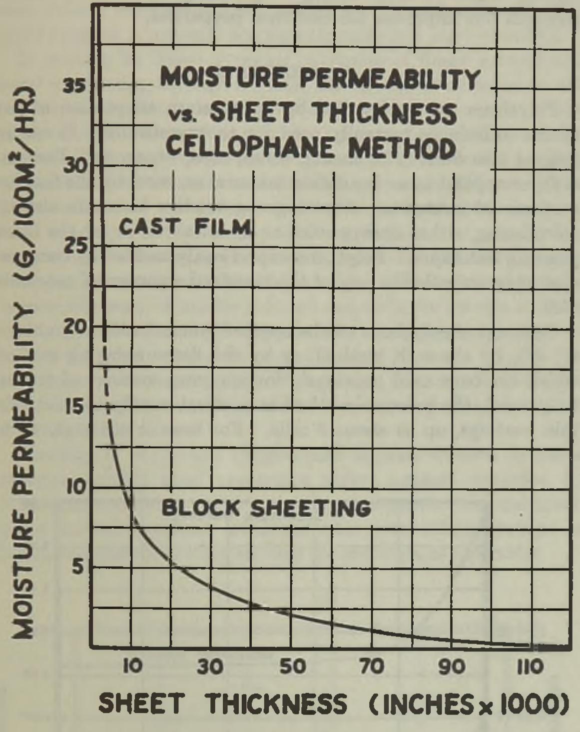

Figure 10. Relation of Moisture Permeability of Polythene to Thickness of Sheet

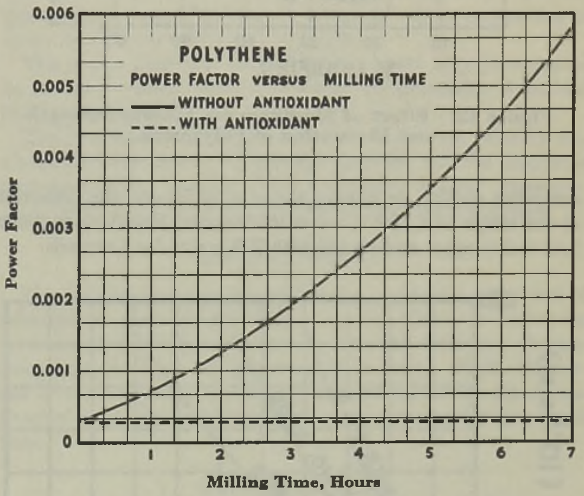

Figure 11. Effect of Milling Time of Polythene on Power Factor

### COMPATIBILITY AND COMPOUNDING

The compatibility of polythene with certain materials follows:

| In All Proportions | In Limited Proportions |
|---|---|
| Raw natural rubber | Neoprene GN |
| Gutta-percha | Butadiene-acrylonitrile rubbers |
| Butyl rubber (GR-I) | Thiokol FA organic polysulfide |
| Buna S (GR-S) | Paraffins |
| Polyisobutylene | Coumarone-indene resins |

Compatibility in general was determined by milling the ingredients together to a homogeneous mixture, molding a test slab from the product, and bending the slab. The development of a white mark at the bend indicates separation of the ingredients and, thus, incompatibility. Exudation from the test slab also is evidence of incompatibility.

As would be expected from its structure, polythene blends with aliphatic hydrocarbons of large molecular weight. The compatibility is sometimes improved by the presence of combined chlorine in the latter. Compatibilities vary somewhat with the source and type of polythene. Paraffin and, to a lesser extent, mineral oil have limited compatibility with polythene; they exude when present beyond certain proportions. The paraffins of larger molecular weight are the more compatible. The solubility limits for paraffin wa x (melting at 56–58° C.) and mineral oil with one particular polythene tested are approximately 15 and 3.5%, respectively, and beyond these limits they exude (Figure 12).

Many additives, even though compatible, lower the tensile strength. Nevertheless, for specific uses (e.g., where greater flexibility is required) modification with these additives may be advantageous. Figure 13 gives a general indication of the effect of certain modifiers on the rigidity of polythene. This property was measured by a method developed in this laboratory, which

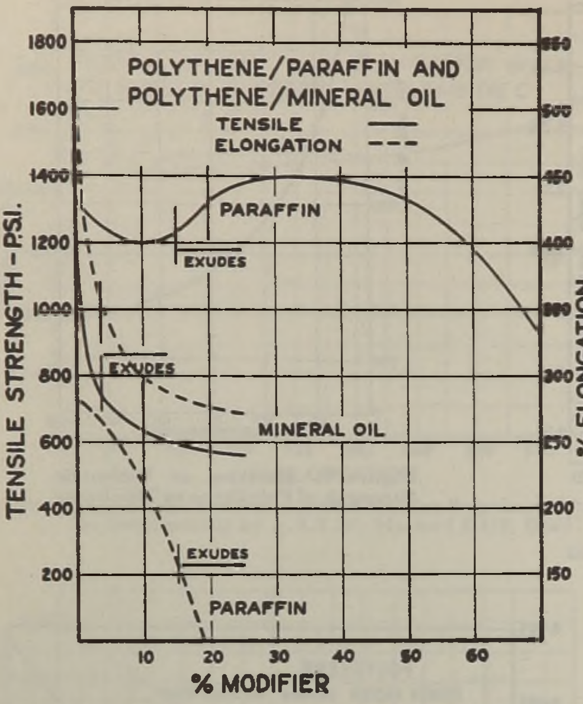

**Figure 12. Effect of Modifiers on Tensile Strength and Elongation of Polythene**

comprises reading, in hundredths of a millimeter, the deflection of the center of a disk 4 inches in diameter, placed on supports 1.62 inches apart and loaded with 700 grams for 5 seconds.

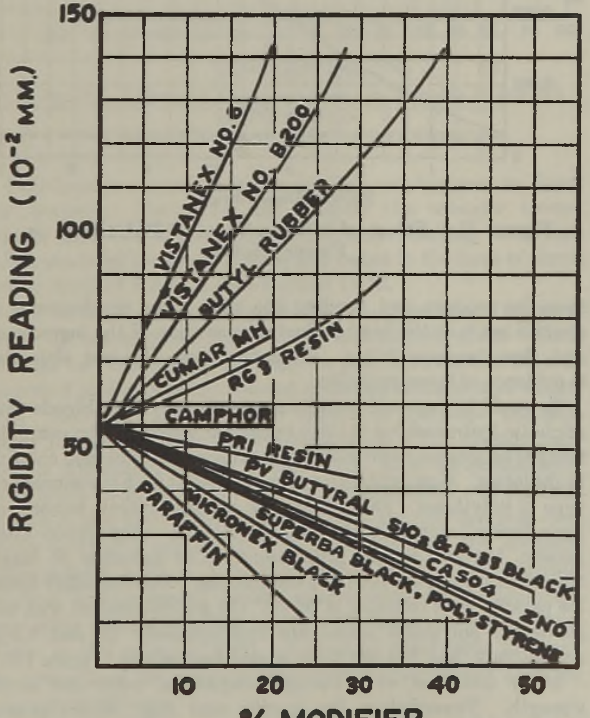

**Figure 13. Effect of Modifiers on Rigidity of Polythene**

R63 resin is a product of Resinous Products and Chemical Company; PRI is an experimental ether resin.

Table VI. Basic GR-I and GR-S Formulas (in Parts by Weight)

| | |
|---|---|
| GR-I | 100.0 |
| ZnO | 5.0 |
| Sulfur | 1.5 |
| Tuads (tetramethylthiuram disulfide) | 1.0 |
| Rotax (mercaptobenzothiazole) | 0.5 |
| Stearic acid | 3.0 |
| Clay | 50.0 |
| Cumar MH 1½ (cumarone-indene resin) | 10.0 |
| Polythene | As required |
| | |
| GR-S | 100.0 |
| Neozone A (antioxidant) | 2.0 |
| ZnO | 5.0 |
| Cumar MH 1½ | 20.0 |
| Paraffin (m.p. 55–57° C.) | 2.0 |
| Heliozone | 2.0 |
| Kalvan (calcium carbonate) | 60.0 |
| Stearic acid | 0.5 |
| Sulfur | 2.5 |
| Thionex (accelerator) | 0.6 |
| 2-MT (accelerator) | 1.25 |
| Polythene | As required |

In the case of white GR-I and GR-S rubber formulations (Table VI), adaptable to electrical use and having relatively low tensile strengths, the addition of polythene improves both electrical and tensile properties (Figures 14, 15, and 16). The addition of polythene to mixtures containing carbon blacks and having higher tensile strengths generally lowers the tensile strength but improves the electrical properties.

### APPLICATIONS

Polythene can be handled by appropriate adaptation of any of the techniques normally used for thermoplastics. It can be formed into films (*17*), sheets, tubes, rods, tapes, and filaments (*16*), or applied as an insulating material on wire, by the familiar methods of extrusion. Sheeting can readily be made also by calendering, either unsupported or upon fabric, or by the block pressing technique. Polythene can be easily molded by compression or by injection in any of the standard commercial machines (*18*).

Coatings of polythene can be applied from solution or emulsion (*1, 11*), by the melt method, or by the flame spraying method which has been used previously for applying coatings of metals. In general, the solution method is applicable only to relatively thin coatings, up to about 3 mils. For heavier coatings, up to

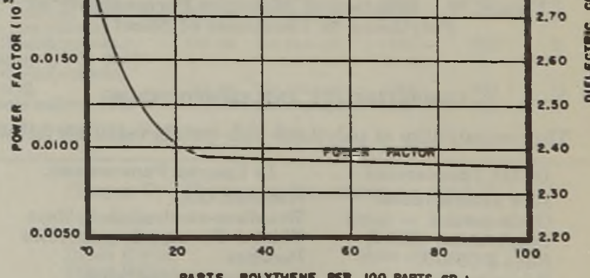

**Figure 14. Effect of Addition of Polythene upon Power Factor and Dielectric Constant of GR-I**

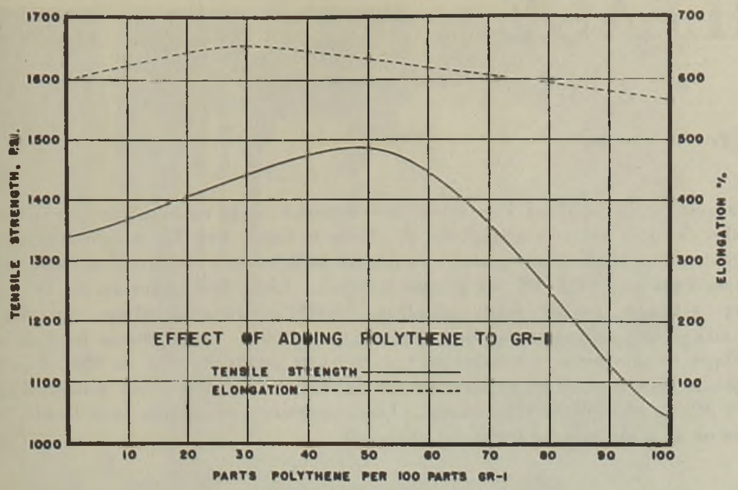

**Figure 15. Effect of Addition of Polythene upon Tensile Strength and Elongation of GR-I**

about 20 mils, the flame spraying technique can be used, and even thicker coatings can be applied by the melt method. The latter requires a material having extremely low melt-viscosity.

In coating by flame spraying, particles of finely ground material are passing through a flame, and are either softened on the surface or completely melted before they impinge on the article to be coated. Successive particles impinge on those previously deposited before either is solidified, and thus continuous coatings are obtained which are so free from microscopic holes that a Tesla coil shows a coating on metal to be entirely nonporous. Such coatings have been deposited on metals, and may be deposited also on wood, glass, brick, plastics, and even paper. They are extremely resistant to corrosion. While pure polythene is quite adherent, it has been found desirable, for service of some types, to add a more adhesive resin to the polythene. For example, the admixture of polyvinyl butyral causes a marked improvement in adhesion, even though the two materials do not possess characteristics which would lead one to believe that they are compatible.

Coatings of polythene compositions applied to steel by flame spraying exhibit good protective action against corrosion by brines and chemicals. For example, coatings on steel test specimens showed excellent adhesion after 9-month immersion in brine, and there was substantially no corrosion of the metal.

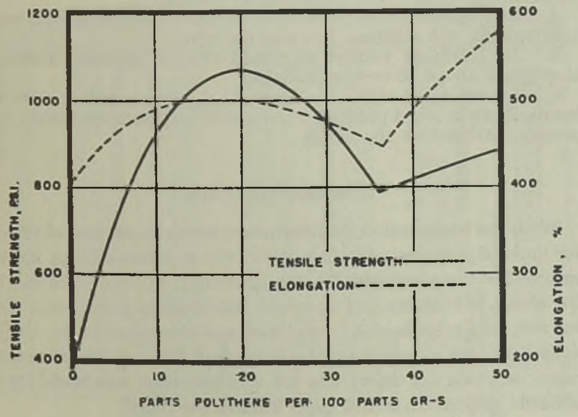

**Figure 16. Effect of Addition of Polythene upon Tensile Strength and Elongation of GR-S**

The military applications of polythene are chiefly in the insulation of cable and high-frequency accessories (*22*). Even before the war its uses in communication and television applications were progressing from the experimental to the commercial stage, and the material will be widely utilized in the post-war development of high-frequency communication systems.

Since polythene is extremely resistant to many chemicals and solvents, it should find use in the field of chemical equipment as a protective coating on piping, reaction vessels, and containers, and as a gasketing material in contact with various acids, alkalies, and other chemicals. In this laboratory hydrofluoric acid has been stored in bottles made of polythene. Similarly, it is suitable for caps and cap liners (*6*) for containers of corrosive materials.

The low moisture permeability and good water resistance of polythene indicate its suitability for the coating of cloth, paper, wood, brick, and concrete, for the fabrication of containers (for milk and other liquids), and for packaging in general. For the latter purposes the plastic can be employed either as sheeting or as an impregnant for paper (*7, 8, 12*).

The use of polythene as a modifying agent may be expected to contribute useful improvements in the properties of various rubbers, waxes, etc.

The commercial production of polythene in this country was a wartime development for military purposes, and the product is under allocation by the War Production Board. However, small quantities can be obtained for experimental purposes.

## ACKNOWLEDGMENT

The authors wish to acknowledge the invaluable assistance of information made available by Imperial Chemical Industries Ltd. and by the Chemical Department, the Ammonia Department, and the Rayon Department of du Pont. W. M. D. Bryant of the Ammonia Department made many of the determinations of refractive index and coefficient of expansion presented here.

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# MOLASSES STILLAGE

GUSTAVE T. REICH

*Pennsylvania Sugar Company, Philadelphia 25, Pa.*

**Concentrated stillage can be carbonized in a stationary retort in acid or alkaline condition. Low-temperature carbonization not exceeding 700° F. yields a hard, brittle, nonhydroscopic product. The stillage treated with alkali metal compound at 8.5–9 pH yields the softest carbonized product; an acid stillage of 4–4.5 pH is the hardest. Lime has a tendency to give the densest product; stillage treated with alkaline metal compound gives the most porous, while the density of the acid char lies between the other two. Continuous feeding of the concentrated stillage to the retorts results in the densest product. Up to 650° F. the loss of organic nitrogen is very low. The separation of potassium sulfate from ammonium chloride by means of dilute alcohol is very sharp. Low-temperature carbon is suitable for chicken feed purposes or as a substitute for wood charcoal.**

DISTILLERIES processing molasses are frequently confronted with the problem of disposing of stillage. From an engineering standpoint the conversion of stillage to a marketable form has been solved, but from an economical standpoint much remains to be done. Values recoverable from the stillage depend upon the quality of raw material processed. It may be blackstrap molasses from Cuba, Puerto Rico, or the Hawaiian Islands, or so-called high-test molasses. Analyses are given in Table I.

The value of the stillage depends upon its organic matter, which is mostly nonsugars, and inorganic compounds such as potash ($K_2O$) combined with chloride, sulfate, and organic compounds. For the recovery of these organic nonsugars, the usual procedure is spray or drum drying of the concentrated stillage. If the yeast has not been extracted, the stillage will contain vitamins such as riboflavin, niacin, and pantothenic acid. The latter is also present in cane molasses, and according to Jukes (*3*), Cuban molasses sometimes has as little as 5 micrograms of that compound per gram. Hawaiian has 70 to 100, while Louisiana has 70 to 80 micrograms.

The first step in recovering values from the stillage consists of concentrating it in multiple-effect evaporators. It has been found that acid stillage with a hydrogen-ion concentration of 4–4.5 cannot be concentrated economically above 33–35° Bé., while alkali stillage may be evaporated to 42–44° Bé.

A process for the low-temperature carbonization of concentrated molasses stillage is described here. Patents have been granted (*6*) on some phases of this work, while another is the subject of a recent patent application. Attention should be called to the fact that the process is not universally applicable. Special local conditions would warrant the use of the process in one form or another, while in other localities it would be uneconomical. Therefore this process should be considered with the above facts in mind.

It has been found that stillage can be carbonized at such a low temperature that most of the organic nonsugars are carbonized practically without loss of nitrogen, and also that the final product is nonhydroscopic and can be handled easily. The aim was to produce a material which could be lixiviated easily and the water-soluble potash compounds separated from the char. A further aim was to convert potassium chloride into sulfate, as the latter is preferable for fertilizer purposes.

## EXPERIMENTAL UNIT

While continuous carbonization would appear to be desirable and is being used by the author, for specific reasons a stationary retort appeared preferable. For experimental purposes a retort was made of $^1/_2$-inch common steel, 1.5 feet wide, 6 feet high, and 8 feet long. It was tapered toward the top and mounted in a firebrick setting heated by two oil burners. No provision was made for agitation, and heating was indirect. The retort setting was such that all the stillage was within the heated area of the retort. Figure 1 shows the complete experimental unit provided with the usual temperature and draft recorders, with a meter for measuring the quantities of fuel oil used. The size of the retort was sufficient for the handling of 150 gallons of concentrated stillage yielding 620 pounds of char and potash. Attention must again be called to the fact that, although the volume of acid and alkaline stillage was the same, owing to the latter's higher density, more finished product could be obtained from it.

The composition of the organic compounds in the stillage is not uniform, especially if the raw materials come from different localities. Therefore, the yields of carbonized product will vary. However, it has been found that, if the carbonization has been carried out at a temperature not exceeding 650° F., the product will contain practically all of the original nitrogen. The structure of the carbonized product varies, not only on account of the variation in the composition of the organic nonsugars but also on whether it was acid or alkaline, whether it contained lime or was heated rapidly or slowly, and whether the charge was carbonized while the stillage was fed continuously or intermittently to the retort. The final product had the following structural characteristics:

1. Greater density resulted from acid stillage than from alkaline.
2. The presence of lime sometimes yielded a product as solid and hard as a rock.
3. Heating a full charge of stillage resulted in a more porous carbonized product than intermittent feeding.
4. Lixiviation of the carbonized product containing lime was incomplete; the alkaline char was the best.
5. Acid stillage yielded a potash char of greater crushing strength than alkali-treated stillage.
6. An excess of alkali in the stillage, with a pH of over 9, resulted in a finished product which could be powdered merely by pressing it between the hands.

## COMMERCIAL UNIT

With the best conditions determined for an experimental retort for low-temperature carbonization of the molasses stillage, larger retorts for the commercial carbonization of stillage were built. To obtain a uniform and constant temperature throughout the retorts, they were heated by radiated and conducted heat. Radiated heat was supplied by the brick wall forming the compartment in which the retort was set, and provision was made for a suitable circulation of hot gases around the retort.

Figure 2 shows the position of the retort. It lies in a heating chamber separated by a wall from the combustion chamber.

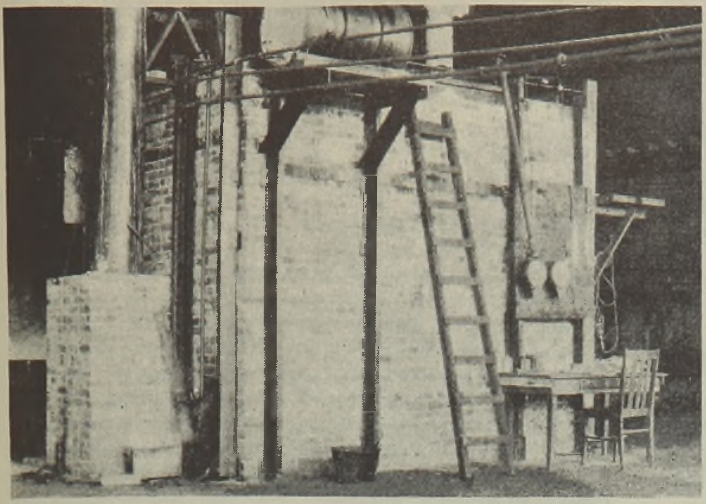

Figure 1. Experimental Furnace for Low-Temperature Carbonization of Molasses Stillage

These walls radiate heat upon the retort. Portholes are provided in these walls which, in combination with the proper flues, enable the production and control of the desired gas circulation as shown in Figure 3. The gas circulation affords the principal control of the temperature in the retort, and this circulation is regulated mainly by the number, size, and position of the portholes, and in part by dampened flues. These factors vary, therefore, with changes in the size and shape of the retort and with variations in the maximum temperature desired.

Because of the forward flaring shape of the retort, provision has to be made to supply more hot gases around the forward portion of the retort. This is accomplished by the arrangement of the portholes, and experience showed that in general the total area of the flue openings should be at least twice the total area of the portholes per partition wall.

Further details of the retorts are shown in Figure 4, where the individual flue gases in the back of the furnace are led into a main header. Flue outlets in the front are not shown. The setting arrangements are pictured in Figure 5 and the retorts in Figure 6. As the concentrated acid stillage had a pH of 4 to 4.5 and the alkali stillage of 8 to 8.5, and since the carbonization temperature was below 700° F., common cast iron retorts were used. Each retort consists of three sections. The over-all dimensions of the retorts are 5 feet high and 15 feet long. The width varies since the retort is tapered; it is 18 inches wide in front and 12 inches in back, and is closed. The front is provided with a door, supported on hinges so that at the end of the run the full charge can be pulled out. The retorts are somewhat similar to Koppers coke ovens.

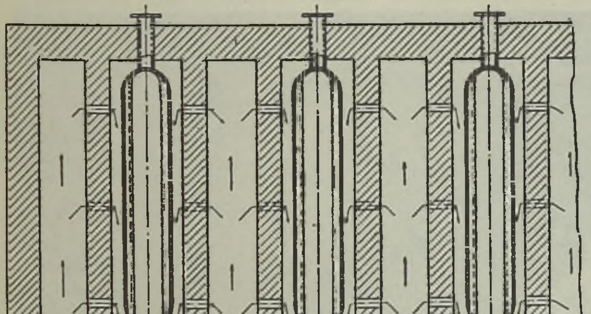

Figure 2. Transverse Sectional Elevation of Retorts

During carbonization the stillage has a tendency to foam, and this foaming again depends upon the quality of the molasses fermented and whether it was treated with an alkali metal compound or not. Other factors which must be considered during low-temperature carbonization are the change in the consistency of the product. No matter what temperature is employed or how rapidly the heat is applied, the stillage foams a great deal, shrinks after foaming, and then goes through a plastic stage before it becomes solid and carbonized.

The potash char can be removed from the retorts in large lumps which, after standing for some time in air, break up into sizes of 3 to 8 inches. The yield of this char is 4.5 pounds per gallon of concentrated stillage of 33° Bé. It required approximately 41 hours per charge and, by producing 129,260 pounds of potash char, the yield per charge averaged 1235 pounds. The carbonized stillage char contained:

| | |
|---|---|
| Total nitrogen | 1.87% |
| Water-insoluble nitrogen | 1.69 |
| Water-soluble nitrogen | 0.18 |
| Total potash ($K_2O$) | 15.44 |
| Water-soluble potash ($K_2O$) | 15.10 |
| Carbon | 32.57 |

Calculating the yields on a unit basis: 1 ton of molasses (168 gallons) yields 730 gallons of beer, 84 gallons of concentrated stillage, and 378 pounds of potash char.

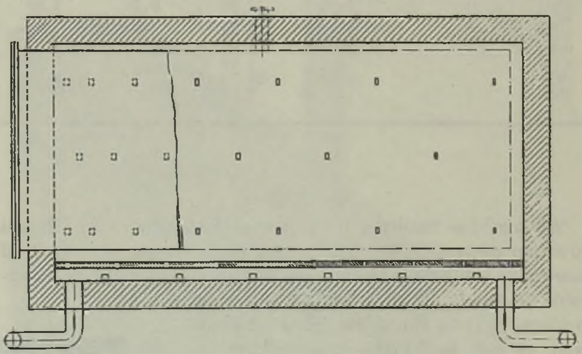

Figure 3. Longitudinal Sectional Elevation of Heating Chamber

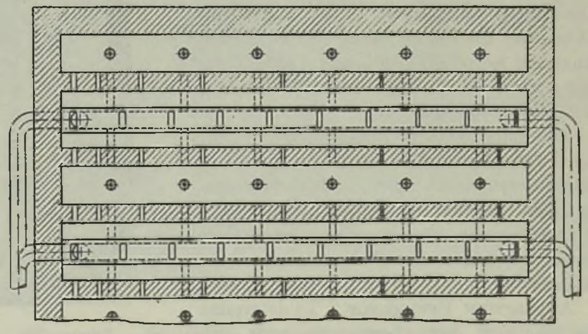

Figure 4. Sectional View of Flue Outlets

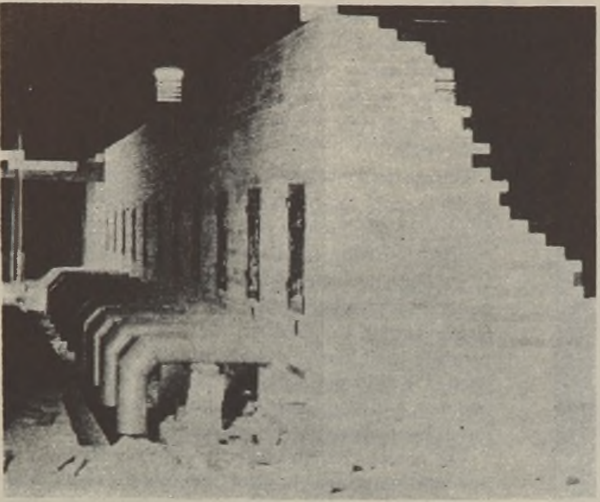

Figure 5. Flue Arrangement

Table I. Composition of Raw Materials Used in Manufacture of Molasses Alcohol

| | Cuba | Hawaii | High Test | Beet (Mich.) |
|---|---|---|---|---|
| °Brix | 82.70 | 86.10 | 84.30 | 86.80 |
| °Baumé | 43.77 | 44.91 | 44.53 | 45.24 |
| Sp. gr., 20/20° C. | 1.4328 | 1.4492 | 1.4437 | 1.455 |
| Sucrose, % | 35.53 | 27.89 | 16.93 | 48.43 |
| Invert sugar, % | 15.77 | 15.55 | 58.33 | .... |
| Raffinose | ..... | ..... | ..... | 1.28 |
| Total sugars, % | 51.30 | 43.44 | 75.26 | 49.71 |
| Nonsugars, % | 31.40 | 42.66 | 9.04 | 37.09 |
| Ash, % | 9.50 | 12.91 | 1.93 | 10.95 |
| Water, % | 17.30 | 13.90 | 15.70 | 13.20 |
| Ash composition, % | | | | |
| $K_2O$ | 45.91 | 25.55 | 49.20 | 57.01 |
| $Na_2O$ | ..... | 2.60 | ..... | 7.26 |
| CaO | 16.12 | 19.08 | 0.10 | 1.69 |
| MgO | ..... | 11.35 | ..... | 0.59 |
| $Fe_2O_3 + Al_2O_3$ | 1.53 | 0.45 | ..... | .... |
| $SiO_2$ | 3.78 | 3.08 | ..... | .... |
| Cl | ..... | 1.27 | ..... | 2.78 |
| $SO_3$ | 15.05 | 20.70 | ..... | 8.95 |
| $P_2O_5$ | ..... | 2.05 | ..... | 3.08 |

## CHAR

When sold as fertilizer, the char is evaluated by its potash and nitrogen contents; the high percentage of carbon is considered merely as a filler. Therefore experiments were made to determine the possibility of using this carbon in poultry feed as a substitute for wood charcoal, as well as for the production of activated carbon.

The first step in the recovery of the low-temperature carbon consisted of leaching the finely or coarsely ground char (*8*). When dry the leached char, free of potash, analyzed as follows: moisture 4.64%, volatile matter 47.85, fixed carbon 41.80, ash 5.71 (total 100%).

The main requirements for a char to be used for poultry feed purposes are: high gas adsorption efficiency, high carbon content, no tendency to discolor the feed, and high crushing strength. Experiments were made to ascertain these qualities in the stillage char and the results are as follows:

Adsorption Efficiency. To determine its efficiency, comparisons were made with other carbons by using carbon dioxide gas. Coconut char was found best, then stillage, wood charcoal, and bone char.

Carbon Content. The various chars analyzed as follows (*5*):

| | Coconut | Wood | Bone | Stillage |
|---|---|---|---|---|
| Moisture | ... | ... | ... | 4.64 |
| Volatile matter + fixed C | 97.86 | 97.76 | 9.30 | 94.25 |
| Ash | 2.14 | 2.24 | 90.70 | 5.75 |

Discoloration. The milling companies desire charcoal which will not discolor the feed. Although the method of testing the charcoals is crude, it appears to be satisfactory since some mills are using it regularly. Ten grams of the carbon are placed in a tin can, 4 inches in diameter and 3 inches high, which contains six ball bearings weighing 90 grams. The can is provided with a tight cover and moves rapidly two hundred times in a swirling motion. The crushed charcoal is screened through a 100- and 200-mesh screen, and the fines are mixed with chicken feed and rolled in a ball mill. The degree of coloration of the stillage feed with the various charcoals are as follows: coconut charcoal best, followed by molasses stillage char, bone char, and wood char.

Crushing Strength. The method of Knowles (*4*) for crushing carbons has given satisfactory results. The results of screening the chars up to 50, 100, 200, or above 200 mesh are:

| Mesh | Coconut | Wood | Bone | Stillage |
|---|---|---|---|---|
| Up to 50 | 91% | 55% | 65% | 73% |
| 50 to 100 | 4 | 10 | 17 | 11 |
| 100 to 200 | 3 | 10 | 8 | 9 |
| Above 200 | 2 | 25 | 10 | 7 |

These results show that the stillage char has a greater crushing strength than wood and bone char.

## BY-PRODUCTS

During the low-temperature carbonization not only gas and tarry matter are driven off, but also large quantities of water. As the concentrated stillage had a density of 33–44° Bé., the water content of the tars was 50–75%. The vapors leaving the retorts around 500° F. pass through a standpipe of conventional design. A blower forces them through a water scrubber which reduces the vapor temperature and precipitates most of the tar and light oils which are collected in a tank as shown in Figure 7.

## CONVERSION OF POTASSIUM CHLORIDE TO SULFATE

The potash ($K_2O$) in the molasses is present as sulfate (25–30%) and chloride (25–40%), and is combined with the organic nonsugars in the amount of 25–40%. If the recovery of the car-

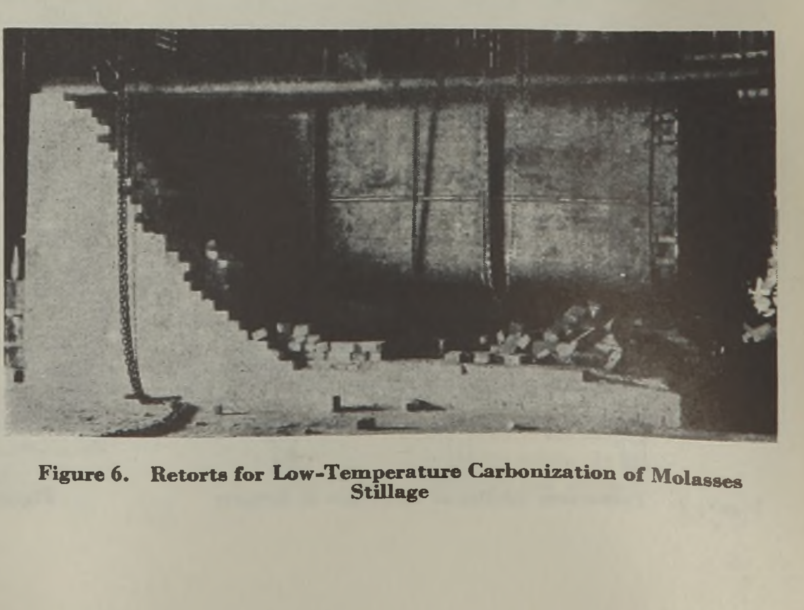

Figure 6. Retorts for Low-Temperature Carbonization of Molasses Stillage

bon is contemplated, the potash must be removed by lixiviation (7). During low-temperature carbonization some of the potash is converted into carbonate, and the lixiviated potash may be similar to the ash obtained by incinerating the stillage.

In some localities the potash is not desired as chloride and carbonate; in fact the latter, being alkaline, has a detrimental influence upon crops and fruit trees. Therefore the problem was to find a process whereby all the potash could be converted into sulfate without expensive chemicals and equipment. At first it appeared necessary merely to treat the potassium chloride, carbonate, or potash, combined with organic matter, with sulfuric acid, thereby liberating hydrochloric acid (*1*) and converting the potash salts to sulfate. However, the difficulties encountered in disposing of such large quantities of hydrochloric acid and the purchase of sulfuric acid for an inexpensive chemical such as potassium sulfate made this procedure appear prohibitive. Other possibilities suggested were the treatment of the potash salts with ammonium sulfate. A similar process with sodium chloride was described by Hochberger (*2*).

It appeared more economical to convert the potash salts to sulfate by treating with ammonium sulfate, according to the equation:

$$2KCl + (NH_4)_2SO_4 = K_2SO_4 + 2NH_4Cl$$

The ammonium sulfate, as purchased, is sold on its nitrogen content; therefore the sulfate ion to be used in this process could be obtained free. Another apparent advantage was that the ammonium chloride could be marketed much more easily than hydrochloric acid.

According to Seidell (*7*) potassium sulfate is less soluble in cold water than ammonium chloride. Therefore it appeared that their separation would not offer a serious problem. However, it was found that in low-temperature carbonization not all organic compounds are carbonized, and upon treatment with water these uncarbonized materials dissolve, impart a coffeelike color, and prevent a smooth separation of potassium sulfate from ammonium chloride. If present in small quantities, these organic compounds have a tendency to increase the fluxing properties of the ammonium chloride during the galvanizing operation, and some firms prefer it to the white ammonium chloride crystals.

## SEPARATION WITH DILUTE ETHANOL

Experiments with ethanol showed that the separation of potassium sulfate and ammonium chloride is very sharp and that products of high purity are obtainable. The solubilities of potassium sulfate in ethanol of specific gravity 0.939 at 140° F. is 0.92 part in 100 parts of solvent; 30.1 parts of ammonium chloride are soluble in the same amount of solvent. At first it appears that the cost of denatured ethanol is prohibitive. Obviously prewar prices are to be considered. Alcohol recovery plants are usually operated at such high efficiency that the loss of solvent is not very great, especially when it has an alcohol content of 45–55% by volume.

The process for the double decomposition is as follows: After the low-temperature potash char is crushed to 20-mesh size, it is lixiviated on the countercurrent principle for the separation of carbon and potash salts. To the potash liquor at a specific gravity of 1.15–1.2 is added ammonium sulfate, preferably in saturated solution, exceeding somewhat the stoichiometric quantity required. The reaction is rapid, and 30–35% of the potassium sulfate is precipitated in 99.5% pure form. The first crop of potassium sulfate is separated by centrifuging, and the mother liquor is concentrated until a specific gravity of 1.25–1.35 at 180° F. is attained. The specific gravities depend upon the water-soluble organic compounds which have a retarding influence upon the crystallization. The reverse takes place in the manufacture of sugar where the inorganic salts, having so-called mellasigenic properties, retard the crystallization of sugar and thus result in the formation of molasses.

When the proper specific gravity has been attained, the solution is cooled with water and agitated; this treatment precipitates most of the potassium sulfate and ammonium chloride. The crystals also contain some water-soluble organic matter and low-temperature tar and oils. Most of the latter is found in the mother liquor with the excess of ammonium sulfate, some potassium and sodium sulfates, and ammonium chloride. The mother liquor at proper concentration is returned to the retorts.

The dark precipitate of potassium sulfate and ammonium chloride, freed from the mother liquor, is treated with denatured ethanol having a specific gravity of 0.92–0.94 at 140° F. The great differences in the solubilities of these salts in the solvent permit quick and easy separation. Potassium sulfate of 99% purity remains undissolved, while the ammonium chloride in solution is recovered by crystallization after the removal of the alcohol. The ammonium chloride thus obtained has a purity of 99.5%, and the mother liquor from these crystals, high in organic impurities, is returned to the liquor for char leaching purposes.

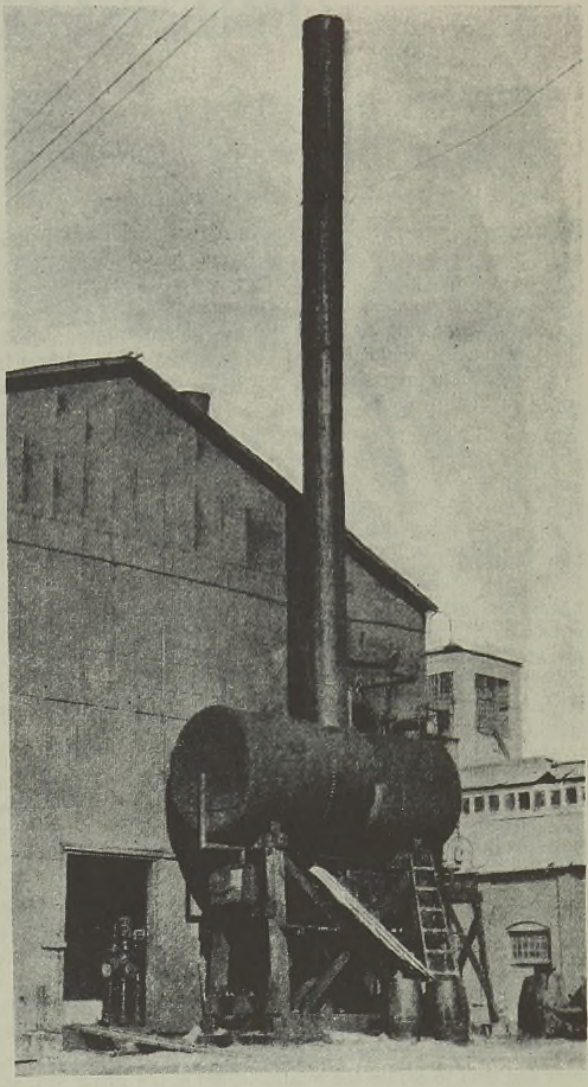

**Figure 7. Scrubber for Tar and Vapors from Low-Temperature Retorts**

The process described above uses ammonium sulfate. Instead of this salt, ammonium nitrate can be employed. The concentration of the liquor in this case will be 1.3–1.45 at 180° F.

## POSTWAR OUTLOOK

The availability of large domestic and foreign supplies of potash salts after the war would not warrant the recovery of the potash and char by concentrating and carbonizing the molasses stillage at a low temperature unless some local or operating condition, especially in the West Indian or other sugar producing countries, offered favorable circumstances. Since the organic nonsugars are of vegetable origin, they yield products similar to those obtained by the low-temperature carbonization of wood. Therefore, the char has possibilities of being used in chicken feed or for other purposes similar to those for which wood charcoal is utilized.

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# HIGH SPEED AGITATOR FOR PRESSURE VESSELS

M. W. KIEBLER

*Coal Research Laboratory*
*Carnegie Institute of Technology, Pittsburgh, Pa.*

The use of pressure equipment in research laboratories has increased steadily over the last several decades to the point of being commonplace. Many investigators have found it possible, through temperature or mass action effects, to increase greatly a reaction velocity or to shift an equilibrium in a desirable direction by conducting the reaction under pressure. In those cases where the reactants occur in a single phase, such as gaseous or liquid solutions, stationary apparatus is often satisfactory. However, if two or even three phases are involved, the rate of reaction can be further increased by providing some means of agitation. At the same time heat transfer between the stirred mass and the vessel wall is materially increased. Numerous devices to mix or stir the contents of a pressure vessel have been reported in the literature. Phillips (*12*) and Groggins and Hellback (*7*) described an arrangement whereby cylindrical bombs are rotated in a constant temperature bath. Other designs which depend on either rotation of the reactor itself or of internal blades for agitation are described by Tongue (*13*), Laupichler (*9*), and Fischer (*5*). Several authors (*1, 4, 11*) have described a shaking or rocking autoclave of a type which has been commercially available for a number of years.

Mechanical difficulties—such as bleeding gases in and/or out of a vessel, attaching gages, condensers, heat exchangers, or safety disks, maintaining constant pressure, etc.—which are encountered with rotating, shaking, or rocking autoclaves can be greatly reduced by an externally powered and internally stirred autoclave (*9, 13*). However, this type of equipment is not entirely without fault. If the vessel is to be used at pressures in excess of several thousand pounds, it is difficult to obtain a stuffing box which will remain gastight for any considerable length of time; and while gas leakage can be reduced by a lantern-lubricated gland, contamination of the reaction mixture with the lubricant then becomes a problem. Power losses, through a packing gland, result in a high initial and operating cost and tend to reduce the rotation speed of the stirrer so that, from the standpoint of agitation and cost, the value of this type of autoclave is often questionable. A 750-cc. autoclave built in the Coal Research Laboratory for service at a pressure of 3000 to 6000 pounds per square inch required $^{1}/_{4}$ horsepower to turn a stirrer at 120 revolutions per minute. Tongue (*13*) described several small laboratory autoclaves of the same type which had similar power requirements. These faults exceed reasonable limits as the size of the autoclave is reduced, since amount of leakage, size of power installation, and amount of agitation will remain fairly constant with wide variation in the volume of the pressure vessel.

A more nearly ideal reactor would be one in which the stirring mechanism and reactants are contained within the same wall. Calvert (*3*) in 1914 obtained a patent on this basic idea which covered not only motor-driven stirrers, but also circulating pumps. MacMillan and Krase (*10*) and Holloway (*8*) published a detailed description of an autoclave in which the stirrer and motor operate under the same gas pressure. Recently (*6*) a method of obtaining agitation by means of a magnetically operated plunger was reported.

This paper describes a totally enclosed motor and agitator, built to operate under more severe conditions with respect to pressure, temperature, and chemical attack than those mentioned above. The stirrer assembly (Figure 1) is constructed as an integral unit which is attached to the bomb head by means of the threaded lower end. The autoclave, shown dismantled as well as assembled to run in Figure 2, was built in these laboratories several years ago to study the hydrogenation of coal in aqueous alkali at temperatures and pressures up to 400° C. 750° F.) and 6000 pounds per square inch. Violent agitation is required in this reaction to produce not only the maximum possible gas-liquid interface, but to prevent the coal particles from fusing together. Sufficient turbulence was obtained in this autoclave by rotating a 2-inch nickel propeller at 1500 r.p.m. in a 750-cc. nickel-lined cylindrical bomb of 3-inch internal diameter.

The body and top closure for the assembly were machined from chrome-vanadium steel (SAE-6145) forgings which were heat-treated and drawn at 900° F. in a salt bath after all machine work had been finished. Data available for this alloy indicate that the resulting product should have a tensile strength of 210,000 pounds per square inch and a Brinell hardness of 470 (48 Rockwell C). The studs were made of a chrome-nickel steel (SAE-3140) drawn at slightly lower temperatures to give a tensile strength of about 200,000 pounds per square inch. The nuts, made of the same alloy except for a lower carbon content (SAE-3120), were carburized for surface hardness. To reduce contamination of the bomb contents, the interior of the assembly was given a thick coat of silver and burnished. The top closure was made up against an unconfined copper gasket which had an internal diameter of 4 inches. Silver gaskets were used between the assembly and head and between the head and the reactor body. A tight-fitting copper condenser on the neck of the assembly served to remove the heat which flowed up from the heated reactor. Six nickel disks were attached to the nickel stirrer shaft to create turbulence and expedite heat removal.

All parts of the electrical system had to be resistant to attack from hydrogen, water, and any organic vapors which might be formed during the course of a reaction. A shaded-pole 1/30-horsepower motor was obtained (model 123, A. G. Redmond Company), and the outer cover removed. Two bearing supports (Figure 1) were made for the top and bottom of the motor. An Oilite bearing was pressed into each support to take the rotor shaft. It was planned to replace these bearings with graphite bushings if hydrogen or organic vapors should remove the lubricant, but this has never been necessary. The supports were held tightly against the stator ends by two bent bolts which passed through slots at opposite sides of the stator. These bolts were salvaged from the motor parts.

Two stators have given satisfactory service in this apparatus. The first was taken as it came from the manufacturer and was given about six coats of a Bakelite varnish. The second was made by winding Formex wire onto a Redmond stator frame and alternately coating the coils with Heresite varnish (No. L-100) and General Electric varnish No. 1676. Each stator was impregnated by suspending it in a container of varnish which could be placed in a vacuum desiccator. The pressure in the desiccator was then alternately decreased and allowed to return to atmospheric to remove entrapped air. The stator was then drained, allowed to air-dry, and finally baked. After each of several impregnations, the stator was supported in a different position for drying and baking. Any varnish which adhered to the outside diameter of the stator was removed with sandpaper. The assembled motor was tested by allowing it to run under water.

Because this motor has no starter brushes or windings, only one lead has to be taken out through the reactor wall with the other lead internally grounded. However, in this design both leads were brought out so that the motor insulation could be more accurately checked. The leads were made by brazing a copper disk on a short piece of heavy Nichrome wire and slipping a Bakelite disk over the wire on each side. The three disks were then crushed together under a gland nut in the top closure. Both the diameter and thickness of the Bakelite must not be less than that of the copper disk. Nichrome wire was used in preference to copper because of greater strength and stiffness. The resistance to ground through this type of seal (*2*) has always been more than 500,000 ohms.

A coil which serves to remove heat from the motor stator was made by bending a piece of $^1/_4 \times {}^1/_8$ inch mild steel tubing to form a long narrow U, which was then wound into a helix. The two ends were separated 180° apart, bent at right angles to the helix, and dropped through holes at the bottom of the motor compartment where they were made up against the wall with compression cones. The only change contemplated for this autoclave is to increase the internal diameter of tubing used in the coil.

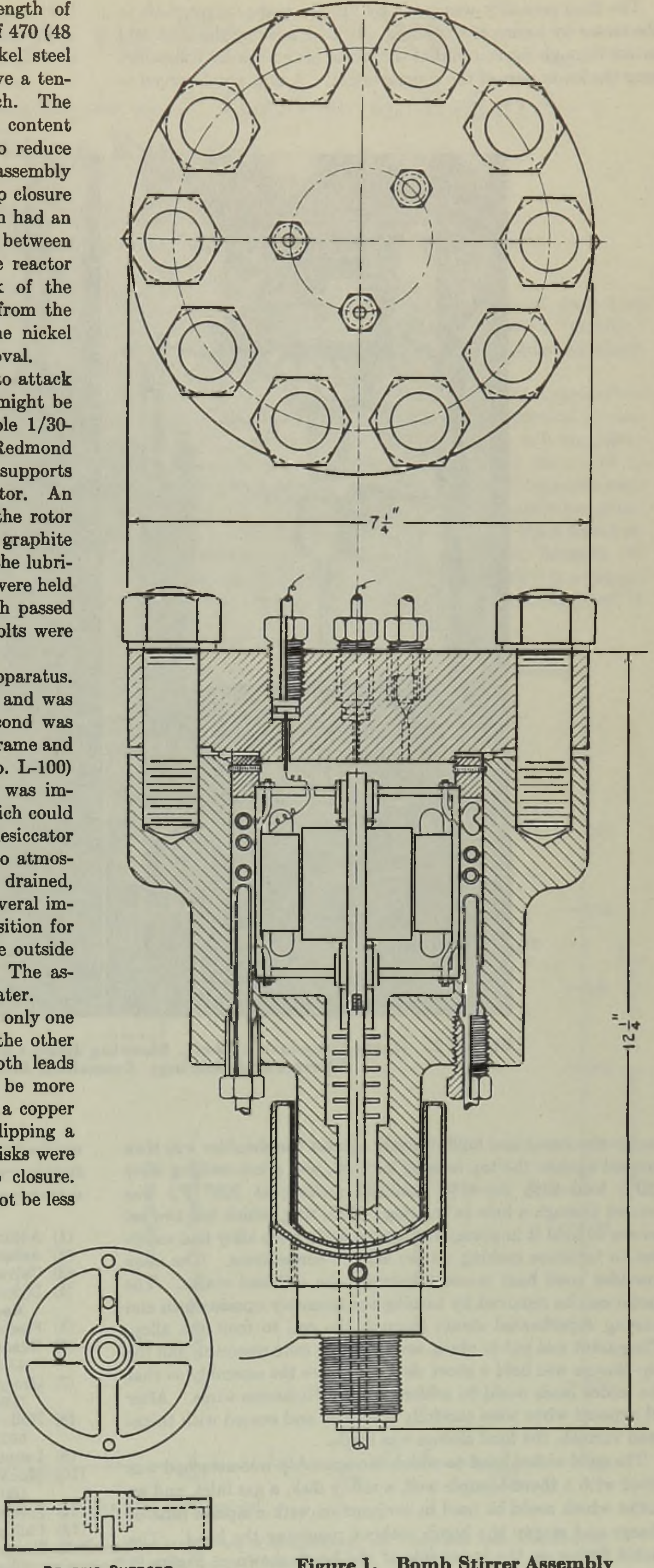

**Figure 1. Bomb Stirrer Assembly**

The final assembly was made by attaching the stirrer shaft to the motor by means of a bushing, and then pushing the shaft and motor through the coil so that the motor rested against a shoulder near the lower part of the compartment. A ring which served to center the motor and hold it firmly against the shoulder was then pressed against the top bearing support, and a low-melting alloy (20% lead–40% tin–40% bismuth, melting at 202° F.) was poured through a hole in the ring. This ring, which has two set screws to hold it in place, was removed after the alloy had solidified to facilitate making up the electric connections. The alloy provides good heat transfer between the coil and stator. The motor can be removed by turning the assembly upside down and passing superheated steam through the coil to melt the alloy. The gasket was put in place, several studs were removed, and the top closure was held a short distance above the assembly so that the motor leads could be soldered to the Nichrome wires. After all exposed wires were carefully insulated and coated with thickened varnish, the final closure was made.

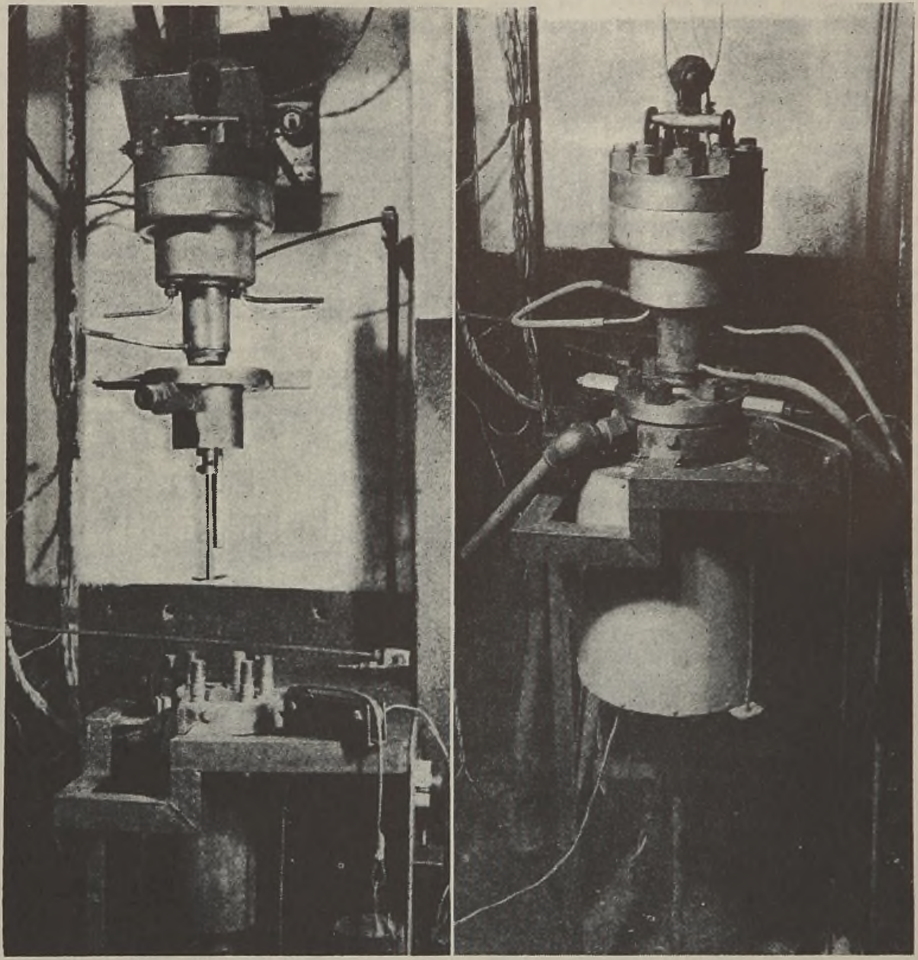

Figure 2. Open Autoclave at Left, Showing Head Construction, Thermocouple Tube, Stirrer, and Bearing; Assembled Autoclave at Right

The solid nickel head to which the assembly was attached was fitted with a thermocouple well, a safety disk, a gas inlet, and an outlet which could be used in conjunction with a siphon tube to charge and empty the bomb without removing the head. The nickel fitting on the lower side of the head, shown in Figure 2, held a graphite bushing to take the stirrer shaft. At various times this fitting has been replaced with a simple packing gland, in which case the pressure in the assembly and bomb were equalized by a connecting tube. The assembly and head, which weighed about 80 pounds, could be conveniently raised above the stationary nickel-lined bomb by a cable and by one fixed and one movable pulley.

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# IMPURITIES in BENZENE

## Nonbenzenoid Hydrocarbons and Toluene in Refined Coke-Oven Benzene

JOHN R. ANDERSON AND CARL J. ENGELDER

*Mellon Institute and University of Pittsburgh, Pittsburgh, Pa.*

ALTHOUGH "nitration benzene" (*1*), the most important commercial grade of benzene, and analytical reagent benzene (*3*) may be relatively impure, very little attention appears to have been paid to the identification of any impurities except thiophene. Stinzendörfer (*8*) concludes that most of the hydrocarbon impurities in a European refined coke-plant benzene are naphthenes, and that the main hydrocarbon impurity is methylcyclohexane. Practical purification methods such as those of Swietoslawski (*6*) throw additional light on the nature of the hydrocarbon impurities, and certain hydrocarbons boiling near benzene have been isolated from high-temperature coal tar (*9*). Whitmore (*10*) states that the only impurity in "nitration benzol" is a small amount of thiophene. Standard methods of test have been devised for nonsulfonatable hydrocarbons (conveniently referred to as paraffins) in benzene (*1*). Results of these tests on nitration benzene indicate a correlation between "paraffin" content and freezing point, the latter being depressed about 0.67° C. per volume % of "paraffins".

An examination of the saturated nonbenzenoid hydrocarbon impurities in nitration benzene seemed to be important in connection with the purification of benzene for use as a secondary physicochemical standard, and in connection with the use of nitration benzene in synthetic, especially industrial, organic chemistry. The sample (I) employed met the specifications for nitration benzene (*1*), and the boiling range and freezing point specifications recommended by the AMERICAN CHEMICAL SOCIETY (*3*) for analytical reagent benzene. We believe sample I is a typical product; it was prepared in a modern by-product coke plant in

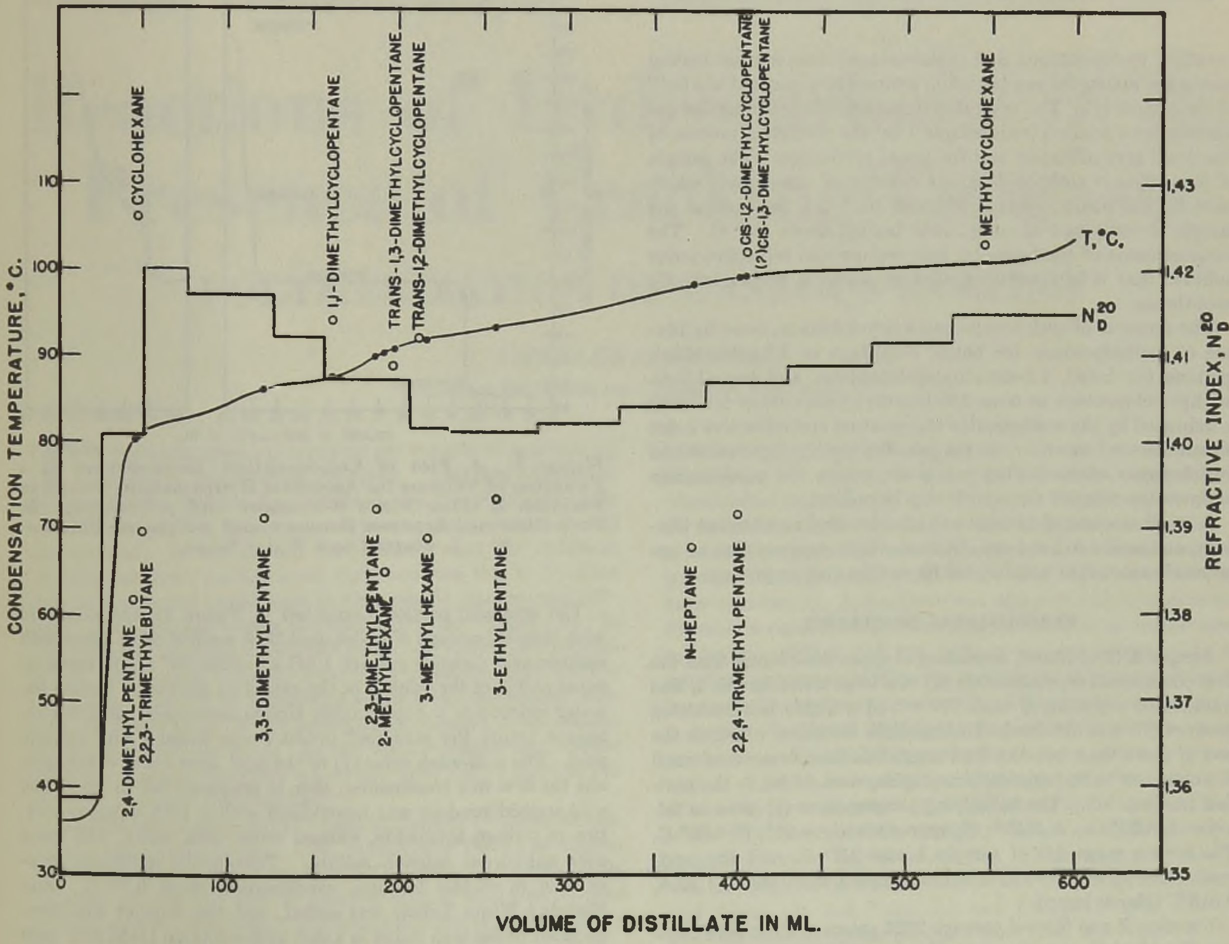

Figure 1. Plot of Condensation Temperature and Refractive Index as a Function of Volume for Saturated Nonbenzenoid Hydrocarbons Plus Some *n*-Pentane

which an efficient batch benzene column is utilized in conjunction with the sulfuric acid refining process.

Figure 1 is a distillation curve, giving condensation temperatures of distillate at 760 mm., of a sample of saturated nonbenzenoid hydrocarbons secured from sample I, plus some $n$-pentane. Figure 1 also presents the results of refractive index ($n^{20}_{D}$) determinations of fractions of the distillate, and the normal boiling points (solid circles) and refractive indices (open circles) of the paraffins, cyclopentanes, and cyclohexanes whose normal boiling points are within the condensation temperature range of the bulk of the sample (*7*). The saturated nonbenzenoid hydrocarbon impurities were secured from sample I by the combined process of fractional crystallization and fractional adsorption. The sample of impurities is composed almost entirely of compounds which have boiling points between 80° and 101° C.; the bulk of the sample is composed of compounds boiling above 90° C. The measurements of condensation temperature and refractive index indicate that it is a complex mixture which is preponderantly naphthenic.

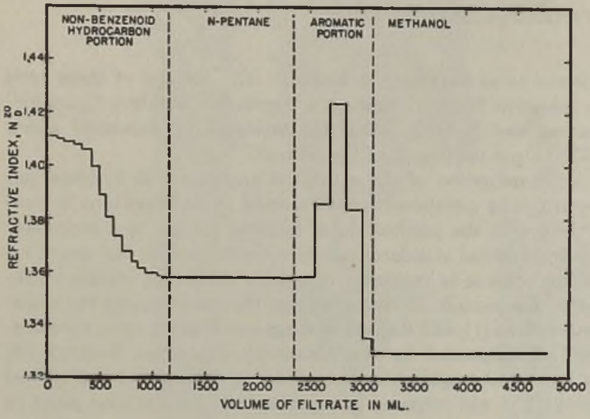

**Figure 2. Results on Separation of Saturated Nonbenzenoid Hydrocarbons from Benzene by Adsorption**

The presence of cyclohexane, methylcyclohexane, 3-methylhexane or 3-ethylpentane (or both), $n$-heptane or 2,2,4-trimethylpentane (or both), 1,1-dimethylcyclopentane, and *trans*-1,2-dimethylcyclopentane or *trans*-1,3-dimethylcyclopentane (or both) is indicated by the condensation temperature and refractive index measurements; however, all the paraffins and cyclopentanes and cyclohexanes whose boiling points are within the condensation temperature range of the sample may be present.

A small amount of toluene was also detected in nitration benzene, and evidence has been obtained which suggests that an appreciable amount of unsaturated impurities may be present.

## EXPERIMENTAL PROCEDURE

Sample A (28.5 liters), consisting of the mother liquor from the first commercial crystallization (*2*) of a large lot of sample I, was fractionally crystallized until 770 ml. of a highly contaminated product (B) was obtained. Intermediate fractions, which at the end of more than two hundred crystallizations became so small in volume as to be practically negligible, were added to the purified fraction (C). The solidifying temperatures (*1*) were as follows: I, 5.20° C.; A, 3.50°; B, approximately −50°; C, 4.68° C. The boiling range (*1*) of sample I was 0.8° C. and the acid-wash color (*1*) 0+. Total sulfur in sample I was 0.0034%; in A, 0.015% (Harris lamp).

Fraction B was filtered through 2825 grams of silica gel (Davison Chemical Corporation, specification 659528-2000) contained a in Pyrex column 250 cm. high and 5 cm. in diameter; the column was constructed from the design of Mair and Forziati (*4*), and their technique (*5*) was used. The sample was followed by the addition of 2175 ml. of $n$-pentane ($n^{20}_{D}$ 1.3575; condensation range 0.2° C.), and then by the addition of 3790 ml. of methanol (tested for hydrocarbons by extraction, with negative results). The refractive indices of the fractions of filtrate withdrawn at the bottom of the column are plotted against the total volume of filtrate withdrawn (Figure 2). When methanol was added to the adsorption column, a red zone immediately developed at the top of the adsorbent. This zone was displaced by the addition of more methanol and was completely removed in the last fractions of the aromatic portion.

The first fifteen fractions (1168 ml.) from the separation by adsorption were combined and fractionated under high reflux in a still with a column (1000 mm. high and 26 mm. in internal diameter) made of Pyrex and packed to a height of 960 mm. with single-turn 4-mm. (approx.) Pyrex helices. The column was jacketed by two other Pyrex tubes concentric with it, and the inner jacket was electrically heated. After the bulk of the $n$-pentane had been distilled, the distillation data in Figure 1 were obtained. A total of 527 ml. of the distillate indicated was distilled from the column, after which the remainder (74 ml.) was carefully distilled from a 200-ml. distilling flask. The condensation temperatures were corrected for pressure fluctuations using 0.045° C./mm. for $dt/dp$. Data for the pure hydrocarbons shown in Figure 1 were taken, with permission, from reports of the American Petroleum Institute Research Project 44 at the National Bureau of Standards.

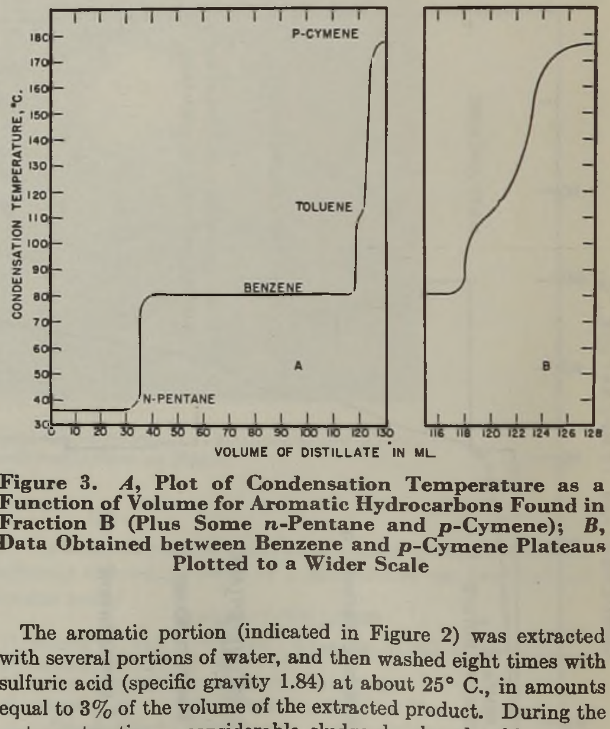

**Figure 3. *A*, Plot of Condensation Temperature as a Function of Volume for Aromatic Hydrocarbons Found in Fraction B (Plus Some *n*-Pentane and *p*-Cymene); *B*, Data Obtained between Benzene and *p*-Cymene Plateaus Plotted to a Wider Scale**

The aromatic portion (indicated in Figure 2) was extracted with several portions of water, and then washed eight times with sulfuric acid (specific gravity 1.84) at about 25° C., in amounts equal to 3% of the volume of the extracted product. During the water extraction a considerable sludge developed; this was removed before the extracted product was washed with sulfuric acid. The acid-wash color (*1*) of the acid layer was 7+ throughout the first five treatments; then it gradually fell to 1+. The acid-washed product was neutralized with a 10% aqueous solution of sodium hydroxide, washed twice with water, and dried over anhydrous calcium sulfate. Twenty-five milliliters of $p$-cymene (a middle fraction, condensation range 0.2° C., from Eastman White Label) was added, and the product was fractionated under high reflux in a still with a column (1150 mm. high and 11 mm. in internal diameter) made of Pyrex and packed to a height of 1000 mm. with single-turn 4-mm. (approximately) Pyrex helices. The distillation data, after the bulk of the *n*-pentane had been removed, are shown in Figure 3*A*. That fraction of the distillate (13 ml.) intermediate between the benzene and *p*-cymene plateaus, indicated in Figure 3*B*, was examined by ultraviolet spectrophotometry with the following results (in per cent): benzene, 33.1; toluene, 32.8; *p*-cymene, 33.3; other material, 0.8.

The following volumes of various products were found in fraction B: saturated nonbenzenoid hydrocarbons, 567 ml. (Figure 1); benzene, 84.3 ml. (Figure 3*A*); toluene, 4.3 ml. (spectrophotometric analysis); loss, 114.4 ml. (by difference).

### DISCUSSION

Since the purpose of this work was to characterize only the saturated nonbenzenoid hydrocarbon impurities, fraction B was not analyzed for thiophene, bromine number, or acid-wash color. However, the behavior of that fraction in the adsorption column (unlike a blank run on the same lot of adsorbent), the large quantity of sludge and acid-wash colors developed during treatment of the so-called aromatic portion, and the large amount of unrecovered material suggest the presence of unidentified impurities; some of these are believed to be unsaturated hydrocarbons.

Fraction B was obtained from 28.5 liters of sample A by purification of the latter through a change of solidifying point equal to 1.18° C. In the absence of a better method of calculation, this information and the volumes of products recovered from fraction B may be used to estimate the order of magnitude of the amounts of impurities in the original nitration benzene. Our estimate (in volume per cent) follows: saturated nonbenzenoid hydrocarbons, 0.6; toluene, 0.004; unidentified, 0.1.

### ACKNOWLEDGMENT

We are pleased to acknowledge the kind cooperation of Wojciech Swietoslawski and William L. Glowacki, both of Mellon Institute. We are also grateful to B. E. Stewart and Frank C. Lauer of Jones and Laughlin Steel Corporation, for furnishing the samples, and to Alberta S. Jones, who assisted with some of the crystallizations. The spectrophotometric analyses were kindly made by N. D. Coggeshall and M. Muskat, of Gulf Research & Development Company.

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Taken in part from a Ph.D. thesis submitted by J. R. Anderson to the University of Pittsburgh. Contribution 552 of the Department of Chemistry, University of Pittsburgh. J. R. Anderson holds an Industrial Fellowship of the Pittsburgh Steel Company at Mellon Institute.

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# Reactions of Hydrocarbons in the Presence of Cracking Catalysts

## POLYMERIZATION OF GASEOUS OLEFINS[1]

**CHARLES L. THOMAS**
***Universal Oil Products Company, Riverside, Ill.***

THE synthetic cracking catalysts are capable of accelerating a variety of hydrocarbon reactions. The type of reaction depends on the hydrocarbon involved and the thermodynamic conditions applied to the system containing the hydrocarbon and the catalyst. It has already been shown that the synthetic cracking catalysts readily sever carbon-carbon bonds in olefins such as octene and hexadecene at atmospheric pressure and 350–500° C. to produce olefins of lower molecular weight (*3*). In one sense this cracking of olefins can be regarded as depolymerization. A classical catalyst—that is, a substance that hastens equilibrium—should be capable of accelerating the reverse reaction, polymerization, if the appropriate changes in thermodynamic conditions are made. In the work reported here, several different synthetic catalysts which had been shown to be active cracking catalysts were studied.

Gaseous olefins have already been polymerized by masses containing silica and alumina. The natural clay known as floridin or Florida earth has been studied extensively. Apparently Gurvich (*8*) was the first to observe that it would polymerize gaseous olefins. This clay is a hydrosilicate of alumina containing both iron and magnesium compounds. This and numerous similar clays, either with or without acid treatment, have received considerable scientific (*2*, *15*, *16*, *21*, *22*, *24*, *26*) and technical (*7*, *10*, *12*, *14*, *19*, *20*, *25*) study as polymerization catalysts. In general the polymers resulting were dimers, trimers, and tetramers, although small proportions of still higher polymers may have been formed. Isobutylene was especially easy to polymerize. Floridin is capable of polymerizing isobutylene at temperatures as low as −100° C. (*15*, *22*). The molecular weight of the isobutylene polymers was found to increase as the temperature was lowered. The higher-molecular-weight polymers were elastomers.

Apparently Gayer (*6*) was the first to report work on a synthetic silica-alumina catalyst for the polymerization of gaseous olefins. His catalyst was prepared by the hydrolytic adsorption of alumina on a silica xerogel. The resulting catalyst contained about 1% alumina. This catalyst produced mainly dimers and trimers under the conditions studied. The same type of catalyst was investigated in considerable detail by Hoog, Smittenberg, and Visser (*9*) and Kazanskiĭ and Rosengart (*13*). Related synthetic silica-alumina catalysts have been described for olefin polymerization (*1*, *4*, *5*, *11*, *18*).

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[1] The four previous articles in this series appeared in *J. Am. Chem. Soc.*, 61, 3571 (1939); 66, 1586, 1589, 1694 (1944).

**Synthetic silica-alumina catalysts as prepared for catalytic cracking will polymerize propylene and the butylenes. Synthetic silica-zirconia catalysts will polymerize butylenes. The three-component synthetic cracking catalysts, silica-zirconia-alumina and silica-alumina-thoria, are active for polymerizing butylenes. The polymers in all cases are liquids boiling mostly within the gasoline range. A $C_8$ fraction, when hydrogenated, had an octane number of 95.3.**

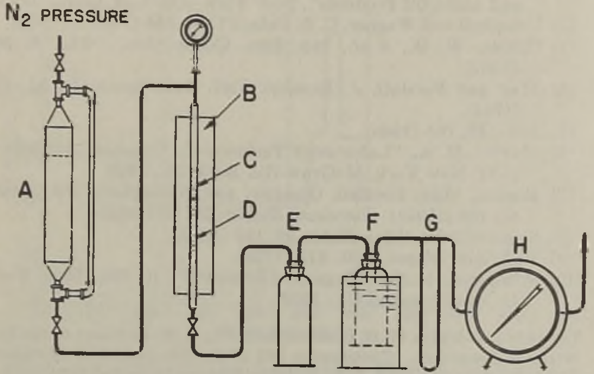

**Figure 1. Apparatus for Polymerizing Gaseous Olefins**

| | | | |
|---|---|---|---|
| *A.* | Pressure vessel with sight glass for liquefied charge | *E.* | Atmospheric pressure receiver |
| *B.* | Thermostated metal block furnace | *F.* | Iced receiver |
| *C.* | 15-cc. silica chips as preheater | *G.* | Flowmeter |
| *D.* | 60-cc. catalyst | *H.* | Gas meter |

The Gayer catalyst is not particularly active as a cracking catalyst. In this work it seemed desirable to investigate the polymerizing ability of synthetic silica-alumina catalysts specially prepared to have a high cracking activity. In addition, synthetic silica-zirconia, silica-alumina-zirconia, and silica-alumina-thoria cracking catalysts and the components silica, alumina, and zirconia were investigated.

The cause or seat of the catalytic activity of either natural or the synthetic catalysts is not clear. The synthetic catalysts are noncrystalline, while the natural clay catalysts are crystalline to x-rays. When properly prepared the synthetic catalysts are more active than the natural catalysts. The synthetic catalysts are known to have surface areas of about 300 to 600 square meters per gram. This would lead us to classify them as adsorption catalysts. Indeed the catalysts are highly adsorptive; however, the silica xerogels without alumina or zirconia are equally adsorptive. It was observed (*6*, *21*) that silica xerogel is not a catalyst for the polymerization of olefins. This caused Gayer (*6*) to make tests on an acid-treated alumina, from which he concluded that the alumina was the real catalyst and the silica was merely a support to distribute the alumina. Gayer also observed that a drop of indicator placed on his 1% alumina-on-silica catalyst gave an acidic reaction. He did not record any connection between this acid nature and the catalytic activity.

### LABORATORY AND PILOT PLANT TESTS

In the laboratory work a number of catalysts were tested to show the presence or absence of polymerizing activity. The pilot plant tests were made on a synthetic silica-alumina cracking catalyst. They provided a sufficient quantity of polymer for rather complete inspection tests.

CATALYSTS. The general methods used in preparing the catalysts have already been described (*17*, *23*). In the present work the precipitated and washed catalysts were dried, formed into 2 × 2 mm. cylinders, and calcined at 500° C.

LABORATORY APPARATUS. The catalyst was placed in a steel tube mounted in a thermostated metal block furnace. The liquefied charging stock was drawn from a calibrated pressure vessel equipped with a sightglass. Small copper tubes were used to connect the charger with the catalyst tube. A needle valve was mounted on the exit of the catalyst tube to control the flow rate. Receivers, a flowmeter, and a wet test meter completed the equipment. Figure 1 is a diagram of the apparatus.

The catalyst and silica chips were placed in the catalyst tube, and the tube was put in the block furnace at reaction temperature. The pressure fittings were then attached to the catalyst tube, and the assembly was tested for leaks with nitrogen at operating pressure. Nitrogen at operating pressure was left in the apparatus. The flow from the charger was then started, and the rate of exit gas was controlled to give an approximately constant flow as indicated by the flowmeter. The charge was determined from the change in level in the pressure charger. The outlet gas was measured by the wet test meter.

The polymer product was stabilized to a distillation temperature of 10° C. to remove dissolved $C_4$ hydrocarbons.

PILOT PLANT EQUIPMENT. The same principle was followed which was used for the laboratory apparatus. The pilot plant was somewhat more complicated in that it was equipped with a pump to feed the liquid charge, an automatic pressure control, and a continuous stabilizer.

CHARGING STOCKS. For practical reasons technical gas mixtures (stabilizer reflux from a Dubbs thermal cracking unit) were chosen as the source of the olefins. The analyses follow:

| Hydrocarbon Constituent | Mole Per Cent | |
|---|---|---|
| | For laboratory tests | For pilot plant tests |
| $C_2H_6$ | 0.5 | .. |
| $C_3H_8$ | 2.8 | .. |
| Iso-$C_4H_8$ | 19.3 | 17.9 |
| *n*-$C_4H_8$ | 28.6 | 30.7 |
| Iso + *n*-$C_4H_{10}$ | 48.8 | 47.9 |
| $C_5$ | .. | 3.5 |

TABLE I. LABORATORY POLYMERIZATION OF $C_4$ FRACTION

(45 kg./sq. cm.; 165° C.; 60-cc. catalyst volume)

| Catalyst type[a] | $100SiO_2$–$11Al_2O_3$ | | $100SiO_2$–$50ZrO_2$ | $100SiO_2$–$5Al_2O_3$–$0.5ThO_2$ | $100SiO_2$–$2Al_2O_3$–$12ZrO_2$ | $SiO_2$[b] | $Al_2O_3$[c] | $ZrO_2$[d] |
|---|---|---|---|---|---|---|---|---|
| Condition | Fresh | Regen. | Fresh | Fresh | Fresh | Fresh | Fresh | Fresh |
| Weight, grams | 28.7 | 28.7 | 38.0 | 25.2 | 35.7 | 25 | 49.3 | 65.9 |
| Feed rate, vol. liquid charge per hr. per vol. catalyst | 7.83 | 8.36 | 7.28 | 7.75 | 6.86 | 6.7 | 6.5 | 7.7 |
| Hours on test | 3 | 14 | 12 | 12 | 12 | | | |
| Polymer yield[e], wt. % $C_4H_8$ charged | 36.6 | 64.3 | 51.8 | 43.2 | 45.7 | | Negligible[f] | |
| Exit gas, mole % | | | | | | | | |
| $C_2H_6$ | 0.6 | 0.8 | 0.7 | 0.7 | 0.7 | | | |
| $C_3H_8$ | 3.4 | 4.0 | 3.7 | 3.5 | 3.6 | | | |
| Iso-$C_4H_8$ | 2.2 | 1.3 | 2.1 | 3.6 | 1.5 | | | |
| *n*-$C_4H_8$ | 34.6 | 23.4 | 28.6 | 30.7 | 31.8 | | | |
| $C_4H_{10}$ | 59.2 | 70.5 | 64.9 | 61.5 | 62.4 | | | |

[a] The catalyst type indicates composition as a ratio of the number of moles of constituents.

[b] Silica xerogel was prepared in the same way as were the other catalysts but without the addition of other oxides.

[c] Activated alumina from Aluminum Ore Company.

[d] Prepared from $ZrOCl_2.8H_2O$ just as if a catalyst were being made but in the absence of the silica hydrogel.

[e] This polymer yield was calculated from the $C_4H_8$ disappearance; in most instances the polymer recovery was somewhat smaller due to mechanical losses.

[f] When no polymer was formed at 165° C. with zirconia, the temperature was gradually raised to 300° C. while maintaining the charging stock flow. No polymer formation was observed.

Table II. Pilot Plant Polymerization of $C_4$ Fraction

(50 kg./sq.cm.; 175° C.; 100 silica–8 alumina, 455 grams)

| Time, Hours | % Removal[a] Iso-$C_4H_8$ | % Removal[a] $n$-$C_4H_8$ | Ratio Iso to $n$-$C_4H_8$ in Polymer[a] | Gas, Standard Liters Charged | Gas, Standard Liters Recovered | Polymer Recovered, liters[b] | Polymer G./g. catalyst/hr. |
|---|---|---|---|---|---|---|---|
| 0–24 | 89.5 | 31.2 | 1.67 | 29,900 | 22,200 | 22.54 | 1.52 |
| 24–48 | 86.5 | 25.2 | 2.0 | 17,750 | 13,600 | 12.67 | 0.855 |
| 48–71[c] | 75 | 20.8 | 2.1 | 15,600 | 12,500 | 8.585 | 0.60 |

[a] Calculated from analysis of inlet and outlet gases.

[b] The yield of polymer calculated from the inlet and outlet gases is somewhat higher. The difference between the calculated polymer and the recovered polymer is presumed to be due to handling losses.

[c] At the end of 71 hours the catalyst weight had increased 4.5%.

Table III. Properties of $C_4$ Polymer from Pilot Plant Test

| Time, hours | 0–16 | 16–24 | 24–48 | 48–71 |
|---|---|---|---|---|
| Vol., liters | 15.58 | 6.96 | 12.67[a] | 8.585 |
| Sp. gr., $d_4^{20}$ | 0.7365 | 0.7267 | 0.7313 | 0.7343 |
| A.S.T.M. distillation, ° C. | | | | |
| Initial b.p. | 37 | 38 | 41 | 46 |
| 10% over | 93 | 98 | 93 | 100 |
| 30% | 116 | 115 | 111 | 113 |
| 50% | 133 | 127 | 124 | 124 |
| 70 | 176 | 170 | 158 | 159 |
| 90 | 258 | 233 | 187 | 188 |
| End point | 294 | 251 | 237 | 234 |

[a] Contains 52.2% $C_8$ hydrocarbons. A.S.T.M. Motor Method octane numbers: crude polymer = 85.3; $C_8$ fraction (95–130° C.) = 85.3; $C_8$ fraction hydrogenated = 95.3.

## EXPLORATORY LABORATORY RESULTS

Preliminary tests were made to see if the catalysts would act as polymerization catalysts and to seek usable reaction conditions. These tests showed that polymerization took place at 165° C., at a pressure of 45 kg. per sq. cm., and at a feed rate corresponding to about 7 volumes of liquefied charge per hour per gross volume of catalyst.

These conditions were used for tests on a number of catalysts. Table I is a summary of the results. From the experience gained in these tests the following observations have been made:

The silica-alumina, silica-zirconia, silica-alumina-thoria, and silica-alumina-zirconia masses were polymerization catalysts.

Individually the silica, alumina, and zirconia did not act as polymerization catalysts.

The catalysts lost activity with use, apparently because of the deposition of carbonaceous material on them.

The catalysts could be regenerated by air at 450–500° C.

The regenerated catalysts were as active or more active than the fresh catalyst.

The catalysts of Table I had different polymerizing activities. The method of catalyst preparation seems to be just as important as chemical composition in preparing active catalysts. Both a suitable preparation method and a suitable composition are necessary to produce an active polymerization catalyst.

As might have been expected from its known activity, isobutylene polymerized more readily than $n$-butylenes under these conditions.

## PILOT PLANT RESULTS

Larger scale tests were made so that the process and the product could be studied in more detail. The conditions of temperature and pressure were nearly the same as those used in the laboratory. The initial feed rate was 8.7 volumes of liquid charge per hour per gross volume of catalyst, but as the activity of the catalyst declined, the feed was reduced so that it was 4.5 at the end of the test. Table II is a summary of the results. Liquid product inspections are listed in Table III. From the data in these two tables the following observations have been made:

The polymerization occurred on the pilot plant scale, very much as would have been expected from the laboratory results.

The catalyst lost activity with use. During the first 24 hours the polymer production rate was about 2.5 times as fast as during the 48–71 hour period.

Again the isobutylene polymerized faster than the $n$-butylenes. As the catalyst aged, it seemed to lose its ability to polymerize $n$-butylenes faster than its ability to polymerize isobutylene.

As the catalyst aged, there was less tendency to form polymers boiling outside the gasoline range. That is, there was a greater tendency for the catalyst to produce dimers rather than higher polymers.

The antiknock quality of the olefinic polymer compared favorably with that produced by other polymerization catalysts.

The antiknock quality of the $C_8$ fraction improved on hydrogenation. This is a property associated with dimers of isobutylene.

Exploratory tests were made on the pilot plant with a propane-propylene fraction containing 18% propylene. Raising the temperature to 250–300° C. at 50 kg. per sq. cm. caused the silica-alumina catalyst to polymerize some of the propylene. The activity of the catalyst seemed to decline faster under these conditions than in the butylene tests. The polymer made under these conditions contained about 10% dimers and some 60% trimers. It will be recalled that Gayer (*6*) and Hoog *et al.* (*9*) obtained polymers containing over 50% dimer by polymerizing propylene. A more detailed study of the propylene polymerization by these catalysts was not made because of the rapid decline in catalyst activity owing to the carbonaceous deposits on the catalyst. It was thought that the rapid decline of the catalyst activity under these conditions might prevent the catalyst from competing with other polymerization catalysts that are known to be able to polymerize propylene while maintaining activity over much longer periods of time.

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# Catalytic Cracking of Cuts from Coastal Crude

D. B. ARDERN, R. H. NEWTON, AND G. L. BARCUS
*Houdry Process Corporation, Marcus Hook, Pa.*

**To obtain basic data on the chemistry of catalytic cracking, four narrow-boiling cuts of Coastal crude oil, having A.S.T.M. midboiling points of 307°, 406°, 543°, and 687° F., were cracked over Houdry synthetic silica-alumina catalyst at conditions of temperature (650–900° F.) and space velocity (0.2–2.0) chosen to obtain variation in the severity of cracking. Dependent variables (pressure and catalyst activity) were controlled to give catalyst deposits equivalent to those obtained in plant operation. The composition of the cracked products was found to vary regularly with the severity of cracking. The greater the severity, the greater was the concentration of aromatics in the cracked product. There was indication that the maximum concentration of cracked naphthenes will occur at moderate cracking severity. The summation of moles of ring compounds decreased as severity increased, indicating a destruction of ring compounds and no net increase in ring compounds formed from chain material. The increase in aromatics was always less than the decrease in naphthenes. Only about 40% of the naphthenes destroyed appeared as aromatics. However, the production of hydrogen was much less than would correspond to simple dehydrogenation of naphthenes to aromatics. At conditions of reasonably constant severity, the total production of olefins increased with increasing boiling range, while total isoparaffin production decreased. Both trends were most evident in the lighter-boiling compounds. The ratio of iso to normal saturated hydrocarbons did not appear to vary appreciably with charging stock or cracking conditions. In the lower-boiling aromatics produced, the weight ratio of benzene:toluene:xylene averaged 1:6:16, although it varied somewhat with conditions.**

WITH the widespread application of catalytic cracking to the production of high-octane motor fuel, there is a growing interest in the chemistry of the cracking process. A previous paper (*1*) gave the chemical composition of gasolines from two catalytic cracking operations and compared them with several thermal and natural gasolines. Other recent investigators (*3*) have studied the reactions occurring when pure compounds are passed over cracking catalysts.

Because Coastal crude oils provide a satisfactory charging stock for catalytic cracking due to the high yield of gasoline in proportion to coke deposited on the catalyst, and also due to the high quality of the motor fuel produced, a series of narrow-boiling cuts from this crude were cracked at several different conditions. The conditions chosen were those commonly used in the Houdry fixed bed cracking process (*2*) and are those in use commercially at the present time. Reasonably complete analyses of the various charge stocks and products were obtained. Because of the rather large number of compounds involved, it is difficult to analyze the results to indicate individual reactions; however, the over-all results, including the interaction of the products and secondary reactions, are of considerable interest. The purpose of this paper is to present the data from these experiments and to show that the composition of the cracked product may be easily controlled over a wide range by control of the cracking variables.

## APPARATUS AND PROCEDURE

Laboratory pilot-plant equipment was used. For all runs, except the low-conversion run at 650° F., the cracking unit was a small case having a capacity of 6.8 liters of catalyst. The catalyst bed was 36 inches deep in a 1-inch annular space obtained by arrangement of concentric tubes. For control of the temperature in the catalyst bed, a liquid commercial heat-treating salt was circulated over the inner and outer surfaces confining the catalyst bed. The temperatures measured by pencil thermocouples located in the catalyst bed were quite uniform throughout the case. Maximum temperatures during the regeneration periods were sometimes 300° F. above the controlled salt temperature, but the catalyst bed was always returned to the desired run temperature before oil was charged to the catalyst.

The run at 650° F. was made in a pilot plant unit having a capacity of 20 liters of catalyst. The internal design of that unit duplicated the configuration of inlet and outlet tubes and multifinned salt cooling tubes, which are standard in commercial Houdry fixed-bed catalytic cases.

Standard laboratory auxiliary equipment was used with both units, including charge pump, rotometers, vaporizer, and product coolers and condensers. The catalysts were synthetic silica-alumina pellet catalysts. They were obtained directly from standard commercial production of Houdry synthetic cracking catalyst. Catalysts of different activities were employed as one of the dependent variables to aid in obtaining desired severity of cracking as described below.

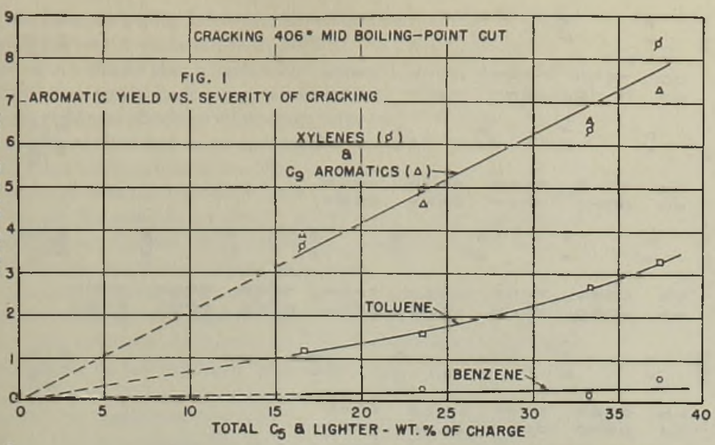
A cyclic operation was used for the experiments in the 6.8-liter case. Each cycle was made as follows: 5-minute evacuation to 1 inch of mercury absolute pressure; 10-minute charging oil at desired space rate and pressure; 5-minute purge with steam and evacuation; 20-minute regeneration with air at 3 cubic feet per minute and 40 pounds per square inch gage. In each run a few cycles were made during which adjustment for proper catalyst deposit was made. Then a number of cycles were run in continuous operation, and samples and data were obtained.

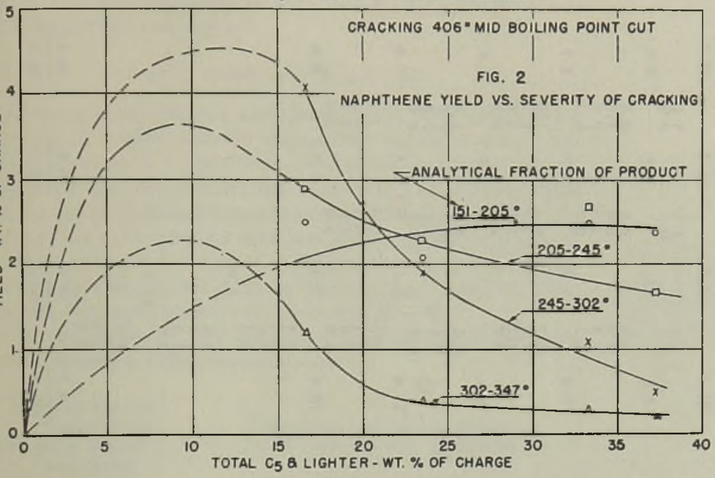
In normal plant practice, cracking conditions are controlled to obtain a catalyst deposit of about 5.0% by weight of the charge at a space rate of 1.0 or 2.5% at a space rate of 2.0. Control of the catalyst deposit is obtained by selection of the catalyst of proper activity and by adjusting the operating pressure. The lower-boiling refractory stocks require a catalyst of relatively high activity and higher operating pressures. As the boiling range of the stock increases, less active catalysts are used, the case operating pressure is reduced, and steam may be added to reduce further the partial pressure of the stock in the case.

On this basis both catalyst activity and operating pressure were varied in these experiments. The maximum case working pressure of 60 pounds per square inch proved to be a limiting factor which resulted in catalyst deposit figures for cracking the 307° F. midboiling-point cut which were 6 to 36% under the average of other cuts at corresponding conditions. It was not necessary to employ steam to prevent excessive catalyst deposits in any of these runs.

The low conversion run made at 650° F. was composed of a single 90-minute period when oil was charged to the catalyst bed, and gas and liquid products were recovered, followed by a regeneration period controlled to obtain essentially total combustion of the catalyst deposit.

Samples of both gas and liquid products were distilled in standard Podbielniak columns, and all light products through *n*-pentane were determined. The liquid product was distilled also in equipment used regularly for making analytical fractions through the gasoline range. This equipment consisted of a 3000-





Figures 1 and 2

ml. flask, electrically heated and connected to a one-inch-diameter Bruun column having forty bubble plates which was operated at a 15 to 1 reflux ratio. The analytical fractions were examined for certain physical and chemical properties on which the paraffin, olefin, naphthene, and aromatic (PONA) contents were determined.

**Charge Stock.** These stocks were obtained from a Coastal crude oil commonly known as Heavy Grade B crude. A typical inspection of this type of crude is given in Table I. Approximately 1600 gallons of the 93% bottoms of the crude were batch-distilled under conditions of good fractionation to give narrow-boiling cuts, each representing about 3% of the crude. Inspections and analyses of the four cuts of the crude selected for this investigation are presented in Table II.

Table I. Inspection of Typical Heavy Grade B Coastal Crude 31° A.P.I. Gravity

| Distillation, ° F. | A.S.T.M. | Vacuum Assay |
|---|---|---|
| Initial b.p. | 180 | 128 |
| 5% over by vol. | 266 | 245 |
| 10% | 358 | 308 |
| 20% | 440 | 410 |
| 30% | 502 | 478 |
| 40% | 556 | 525 |
| 50% | 608 | 620 |
| 60% | 656 | 670 |
| 70% | 702 | 715 |
| 80% | 726 | 825 |
| 90% | ... | 905 |
| 95% | ... | ... |
| End point | 728 | 925 |
| Recovery, % | 87.0 | 91.0 |
| Residue, % | 12.7 | ... |
| Aniline point, ° F. | ... | 167 |
| Characterization factor *K* | ... | 11.5 |

## EXPERIMENTAL DATA

The term "severity of cracking" is used here to give a measure of the relative amount of cracking work done upon the charge stock under the imposed cracking conditions. The measure of severity has been taken as the weight per cent of the charge obtained as $C_5$ and lighter products from the cracking reaction.

The analytical data compiled for each experiment are assembled in Table III, in order of increasing severity of cracking. Variation in severity was obtained by fixing conditions of temperature and space rate as follows: 650° F., 0.2 space rate; 840°, 2.0 space rate; 840°, 1.0 space rate; 900°, 1.0 space rate. The conditions gave an increasing severity of cracking for each charge stock, but the severity was not constant for all cuts cracked at the same conditions of temperature and space rate.

Data are reported in weight per cent of the charge stock. Since the Podbielniak analysis procedure presents results in molal volumes, these were converted to weight per cent using the densities of the compounds. The analyses for hexanes and heavier were converted from the liquid volume percentages, determined analytically, to weight percentages by applying the average density of compounds in each boiling-range cut based on the data published by Ward and Kurtz (*4*).

The conversion from volume to weight basis by that method appeared satisfactory for fractions boiling up to 392° F., since the determined density of the analytical fraction agreed closely with the density calculated for the fraction using the determined volume of each type of organic compounds and the corresponding densities for those compounds at the midboiling point of the fraction. Above 392° F. the weight per cent data are less firm, possibly as a result of errors introduced by the presence of bicyclic compounds which were not identified separately in the analyses.

## EFFECT OF VARIABLES

**Severity of Cracking.** A regular variation between severity of cracking and composition of cracked products was found. Figure 1 shows the increase in production of the lower-boiling aromatics when cracking the 406° F. midboiling-point cut at increasing levels of severity.

Table II. Inspections and Analyses of Charge Stocks

| Cut number | 1 | 2 | 3 | 4 | |
|---|---|---|---|---|---|
| Vol. % of full crude | 10.0–13.0 | 19.2–22.1 | 45.9–48.9 | 66.7–69.6 | |
| Gravity, ° A.P.I. | 46.8 | 39.6 | 32.8 | 27.5 | |
| Distillation, ° F. | A.S.T.M. | A.S.T.M. | A.S.T.M. | A.S.T.M. | Vac. assay |
| Initial b. p. | 290 | 372 | 497 | 657 | 600 |
| 5% over by vol. | 296 | 388 | 527 | 672 | 705 |
| 10% | 298 | 398 | 535 | 676 | 706 |
| 30% | 302 | 403 | 540 | 683 | 710 |
| 50% | 307 | 406 | 543 | 687 | 713 |
| 70% | 313 | 409 | 547 | 691 | 717 |
| 90% | 320 | 417 | 553 | 700 | 725 |
| 95% | 330 | 422 | 558 | 708 | 735 |
| Dry point | 338 | 434 | 561 | ... | ... |
| Aniline point, ° F. | 116.4 | 132.1 | 157.5 | 181.4 | |
| Characterization factor *K* | 11.5 | 11.5 | 11.6 | 11.8 | |
| Chemical analysis, % by wt. | | | | | |
| Paraffins | 25.8 | 3.7 | ... | ... | |
| Olefins | 0.0 | 0.9 | ... | ... | |
| Naphthenes | 59.7 | 80.4 | ... | ... | |
| Aromatics | 14.5 | 15.0 | ... | ... | |

### Table III. Yields (in Weight Per Cent of Charge) from Cracking Coastal Crude

| | 650° F., 0.2 Space Rate | 840° F., 2.0 Space Rate | | | | 840° F., 1.0 Space Rate | | | | 900° F., 1.0 Space Rate | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Cut No. | 2[a] | 1[a] | 2 | 3 | 4[a] | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 |
| Midboiling-point, ° F. | 406 | 307 | 406 | 543 | 687 | 307 | 406 | 543 | 687 | 307 | 406 | 543 | 687 |
| Cracking pressure, lb./sq. in. | 10 | 60 | 25 | 15 | 4 | 60 | 25 | 10 | 3 | 60 | 10 | 7 | 2 |
| Catalyst deposit | 2.2 | 1.4 | 2.1 | 2.2 | 2.4 | 3.5 | 4.6 | 4.5 | 4.7 | 4.7 | 4.9 | 5.0 | 5.1 |
| $H_2$ | | | 0.02 | 0.01 | | 0.02 | 0.004 | 0.01 | 0.04 | 0.07 | 0.06 | 0.06 | 0.06 |
| CO | | | 0.01 | 0.02 | | 0.03 | 0.03 | 0.03 | 0.03 | 0.1 | 0.01 | 0.01 | 0.2 |
| $CO_2$ | | | 0.1 | 0.2 | | 0.04 | 0.2 | 0.3 | 0.2 | 0.6 | 0.2 | 0.1 | 0.0 |
| Methane | | | 0.2 | 0.2 | | 0.6 | 0.6 | 0.2 | 0.5 | 1.6 | 0.7 | 0.7 | 3.4 |
| Ethene | | | 0.3 | 0.2 | | 0.4 | 0.4 | 0.3 | 0.3 | 0.5 | 0.5 | 0.6 | |
| Ethane | | | 0.2 | 0.2 | | 0.6 | 0.4 | 0.3 | 0.4 | 0.0 | 0.2 | 0.6 | |
| Total $C_2$ | | | 0.5 | 0.4 | | 1.0 | 0.8 | 0.6 | 0.7 | 1.4 | 0.7 | 1.2 | 1.1 |
| Propene | | | 1.1 | 1.4 | | 0.6 | 1.1 | 1.6 | 2.4 | 0.7 | 2.2 | 3.1 | |
| Propane | | | 2.4 | 1.4 | | 5.4 | 4.1 | 1.8 | 1.8 | 6.6 | 4.7 | 2.8 | |
| Total $C_3$ | | | 3.5 | 2.8 | | 6.0 | 5.2 | 3.4 | 4.2 | 7.3 | 6.9 | 5.9 | 6.0 |
| Isobutane | | | 7.2 | 5.0 | | 12.1 | 9.5 | 6.6 | 6.3 | 12.3 | 10.4 | 7.8 | 5.4 |
| Isobutene | | | 0.1 | 0.2 | | 0.2 | 0.1 | 0.2 | 0.4 | 0.2 | 0.3 | 0.5 | 0.5 |
| *n*-Butene | | | 1.1 | 1.6 | | 0.5 | 0.8 | 1.5 | 2.1 | 0.5 | 1.3 | 2.4 | 3.4 |
| *n*-Butane | | | 2.0 | 1.0 | | 3.0 | 2.5 | 1.4 | 1.3 | 3.3 | 2.4 | 1.7 | 2.6 |
| Total $C_4$ | | | 10.4 | 7.8 | | 15.8 | 12.9 | 9.7 | 10.1 | 16.3 | 14.4 | 12.4 | 11.9 |
| Isopentane | | | 6.0 | 5.0 | | 9.9 | 8.5 | 5.6 | 6.4 | 9.0 | 7.8 | 6.5 | 5.7 |
| Pentenes | | | 0.6 | 1.1 | | 0.3 | 0.2 | 1.2 | 1.5 | 0.6 | 1.0 | 1.7 | 2.0 |
| *n*-Pentane | | | 0.2 | 0.3 | | 0.5 | 0.3 | 0.7 | 0.5 | 0.5 | 0.5 | 0.7 | 0.5 |
| Total $C_5$ | | | 6.8 | 6.4 | | 10.7 | 9.0 | 7.5 | 8.4 | 10.1 | 9.3 | 8.9 | 8.2 |
| Total $C_5$ and lighter | 16.6[b] | 22.0[b] | 23.6 | 20.0 | 20.4[b] | 37.7 | 33.3 | 26.2 | 28.9 | 42.2 | 37.2 | 34.3 | 36.0 |
| Paraffin | 4.0 | 3.6 | 3.7 | 2.7 | 2.3 | | 3.8 | 3.8 | 4.1 | 3.7 | 4.0 | 3.1 | 3.9 |
| Olefin | 0.1 | 0.1 | 0.3 | 0.6 | 0.7 | | 0.1 | 0.5 | 0.9 | 0.2 | 0.3 | 0.6 | 1.0 |
| Total 104–151° F. cut | 4.1 | 3.7 | 4.0 | 3.3 | 3.0 | 5.8 | 3.9 | 4.3 | 5.0 | 3.9 | 4.3 | 3.7 | 4.9 |
| Paraffin | 3.1 | 1.5 | 2.1 | 3.0 | 3.3 | | 3.0 | 2.9 | 3.8 | 1.9 | 1.6 | 2.3 | 2.4 |
| Olefin | 0.1 | 0.2 | 0.3 | 0.7 | 1.4 | | 0.2 | 0.6 | 1.0 | 0.2 | 0.3 | 0.8 | 1.5 |
| Naphthene | 2.5 | 2.5 | 2.1 | 1.7 | 1.6 | | 2.5 | 2.0 | 2.6 | 1.0 | 2.4 | 1.7 | 2.2 |
| Aromatic | 0.1 | 0.4 | 0.3 | 0.3 | 0.1 | | 0.2 | 0.2 | 0.1 | 0.8 | 0.6 | 0.3 | 0.2 |
| Total 151–205° F. cut | 5.8 | 4.6 | 4.8 | 5.7 | 6.4 | 5.8 | 5.9 | 5.7 | 7.5 | 3.9 | 4.9 | 5.1 | 6.3 |
| Paraffin | 1.7 | 0.4 | 1.1 | 1.1 | 2.1 | | 1.5 | 1.2 | 1.5 | 0.8 | 1.4 | 1.0 | 0.9 |
| Olefin | 0.1 | 0.1 | 0.2 | 0.4 | 1.1 | | 0.2 | 0.3 | 0.5 | 0.1 | 0.2 | 0.5 | 0.6 |
| Naphthene | 2.9 | 1.2 | 2.3 | 1.8 | 2.4 | | 2.7 | 1.7 | 1.9 | 0.5 | 1.7 | 1.6 | 1.6 |
| Aromatic | 1.2 | 1.3 | 1.6 | 0.8 | 0.6 | | 2.7 | 1.1 | 0.9 | 1.9 | 3.3 | 1.3 | 1.3 |
| Total 205–245° F. cut | 5.9 | 3.0 | 5.2 | 4.1 | 6.2 | 5.4 | 7.1 | 4.3 | 4.8 | 3.3 | 6.6 | 4.4 | 4.4 |
| Paraffin | 2.1 | 4.9 | 0.9 | 0.3 | 1.2 | | 0.5 | 1.4 | 1.8 | 3.7 | 0.3 | 0.8 | 1.0 |
| Olefin | 0.1 | 0.2 | 0.2 | 0.4 | 0.9 | | 0.1 | 0.3 | 0.5 | 0.0 | 0.1 | 0.3 | 0.7 |
| Naphthene | 4.1 | 8.6 | 1.9 | 3.1 | 2.0 | | 1.1 | 2.2 | 2.9 | 2.5 | 0.5 | 1.5 | 2.2 |
| Aromatic | 3.6 | 7.1 | 4.9 | 2.0 | 1.2 | | 6.4 | 2.5 | 2.6 | 13.0 | 8.4 | 4.2 | 3.2 |
| Total 245–302° F. cut | 9.9 | 20.8 | 7.9 | 5.8 | 5.3 | 17.4 | 8.1 | 6.4 | 7.8 | 19.2 | 9.3 | 6.8 | 7.1 |
| Paraffin | 0.3 | 8.6 | 0.2 | 0.8 | 0.9 | | 0.3 | 0.8 | 1.2 | 5.8 | 0.4 | 0.4 | 0.7 |
| Olefin | 0.1 | 0.3 | 0.1 | 0.2 | 0.4 | | 0.1 | 0.2 | 0.2 | 0.0 | 0.1 | 0.1 | 0.1 |
| Naphthene | 1.2 | 13.9 | 0.4 | 1.5 | 1.5 | | 0.3 | 1.6 | 1.5 | 2.1 | 0.2 | 0.7 | 0.7 |
| Aromatic | 3.9 | 10.6 | 4.6 | 2.7 | 2.2 | | 6.6 | 3.9 | 3.9 | 10.3 | 7.3 | 4.5 | 4.2 |
| Total 302–347° F. cut | 5.5 | 33.4 | 5.3 | 5.2 | 5.0 | 18.4 | 7.3 | 6.5 | 6.8 | 18.2 | 8.0 | 5.7 | 5.7 |
| Paraffin | | | 2.0 | | | | 1.8 | | | | 2.1 | | |
| Olefin | | | 0.2 | | | | 0.1 | | | | 0.1 | | |
| Naphthene | | | 5.2 | | | | 2.6 | | | | 2.3 | | |
| Aromatic | | | 4.5 | | | | 4.4 | | | | 2.9 | | |
| Total 347–392° F. cut | | | 11.9 | | | | 8.9 | | | | 7.4 | | |
| Paraffin | | | 7.2 | | | | 5.8 | | | | 6.3 | | |
| Olefin | | | 0.2 | | | | 0.2 | | | | 0.0 | | |
| Naphthene | | | 15.6 | | | | 6.5 | | | | 6.7 | | |
| Aromatic | | | 4.2 | | | | 2.6 | | | | 1.9 | | |
| Total 392–437° F. cut | | | 27.2 | | | | 15.1 | | | | 14.9 | | |
| Paraffin | 6.3 | | 0.9 | | | | 0.7 | | | | 0.1 | | |
| Olefin | 1.5 | | 3.5 | | | | 2.1 | | | | 2.7 | | |
| Naphthene | 31.0 | | 1.5 | | | | 0.7 | | | | 0.2 | | |
| Aromatic | 13.4 | | 4.2 | | | | 6.9 | | | | 4.4 | | |
| Total bottoms | 52.2 | 12.5 | 10.1 | 55.9 | 53.7 | 9.5 | 10.4 | 46.6 | 39.2 | 9.3 | 7.4 | 40.0 | 35.6 |
| Total product | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |

[a] No light products data obtained.
[b] $C_5$ and lighter estimated from other data.

Naphthenes boiling below the initial boiling point of the charge likewise show a variation with severity, as plotted in Figure 2. The data indicate that a maximum concentration of lower-boiling naphthenes would be found at a low severity. The highest naphthene yield was obtained when operating at 650° F., but temperature was not treated as an independent variable and these data do not suffice to evaluate the effect of temperature alone. On the hypothesis that the high-naphthene yield is a function of severity, it should be possible to obtain about the same production of naphthenes at higher temperatures if pressure and space rate are adjusted to assure low severity of cracking.

**Boiling Range of Charge.** When cracking under conditions of constant temperature, space rate, and catalyst deposit, the boiling range of the charge stock has a direct bearing upon the production of lower-boiling isoparaffins and olefins (Figure 3). While the variations are pronounced in the $C_4$ range, in the $C_6$ and heavier analytical fractions the boiling range has little or no effect. For the data in Figure 3 the severity varied from 34.3 to 42.2 weight % $C_5$ and lighter.

### RING COMPOUND BALANCES

Data on aromatics and naphthenes, obtained when cracking the 406° F. midboiling-point charge, were converted to a molal basis by means of a correlation of molecular weight *vs.* boiling point from the data of Ward and Kurtz and the determined midboiling points of the analytical fractions. The total moles of ring compounds in the product decreased with increasing severity of cracking as shown in Figure 4. Likewise, the amount of residual ring compounds, which includes unreacted and polymer compounds, decreased rapidly with increasing severity.

The ring balance for the most severe cracking operation follows (basis, moles per 1000 grams of charge):

$$\left.\begin{array}{r}\text{4.70 moles charge}\\ \text{naphthenes}\\ \text{0.96 mole charge}\\ \text{aromatics}\end{array}\right\} \longrightarrow \left\{\begin{array}{l}\text{0.54 mole residual naphthenes}\\ \text{0.53 mole residual aromatics}\end{array}\right\} +$$

$$\left\{\begin{array}{l}\text{0.48 mole lighter naphthenes}\\ \text{1.84 moles lighter aromatics}\end{array}\right.$$

$$\left.\begin{array}{l}\text{4.16 moles charged naph-}\\ \text{thenes destroyed}\\ \text{0.43 mole charged aro-}\\ \text{matics destroyed}\end{array}\right\} \longrightarrow \left\{\begin{array}{l}\text{0.48 mole lighter naph-}\\ \text{thenes produced}\\ \text{1.84 moles lighter aro-}\\ \text{matics produced}\end{array}\right.$$

$$\begin{array}{l}\text{4.59 moles charged rings}\\ \text{destroyed}\end{array} \longleftrightarrow \begin{array}{l}\text{2.32 moles lighter rings}\\ \text{produced}\end{array}$$

Similar data can be tabulated for the other conditions on cut 2 also. In general, only about 50% of the total ring compounds destroyed appeared as ring compounds produced. There appeared to be no gain in ring compounds owing to their formation from chain material. The gain in aromatics was always less than the loss of naphthenes. Only 35–40% of the naphthenes destroyed appeared as lower-boiling aromatics at the condition of greatest severity, and that proportion was less in less severe operation. The amount of hydrogen determined in the cracking products was much less than would correspond to simple dehydrogenation of naphthenes to aromatics.

### COMPOSITION OF PRODUCTS

In Figure 5 the percentage PONA distribution is shown for each analytical fraction obtained in cracking the 406° F. midboiling-point cut at the four conditions used. It is evident that the wide range of severity did not affect radically the characteristic distribution of compounds within any analytical fraction. However, the trends of aromatic and naphthene production pointed out above are apparent. Olefins are most evident in the run at greatest severity, but this is probably due principally to the 900° F. temperature. Beyond the 325° F. midpoint fraction the overlap into the boiling range of the charge stock is evident from the large naphthene concentration present. The bottoms fraction was primarily material boiling above the end point of the charge stock and was composed principally of aromatics and olefin polymer.

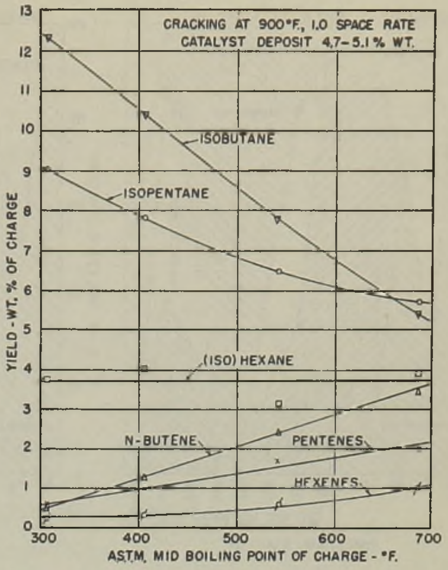


Figure 3. Isoparaffin and Olefin Yields *vs.* Boiling Point of Charge

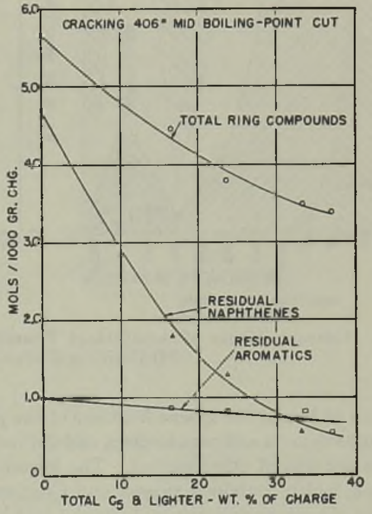


Figure 4. Variation in Ring Balance with Severity of Cracking

Except for the runs made with the 307° F. midboiling-point charge, the distribution of the lower-boiling aromatics was nearly constant throughout the experiments. Benzene production averaged 2.5% of the $C_9$ and lighter aromatics, and toluene production averaged 14.5%. Neither severity nor charge had any effect upon the relative concentration of those compounds. The ratio of xylenes to $C_9$ aromatics was 1 to 1 with the 406° midboiling charge and averaged 2 to 3 using the 687° midboiling cut. The ratio showed slight increase with increasing severity. The average weight ratio benzene:toluene:xylene was 1:6:16, but it varied appreciably in individual runs. Examination by super-

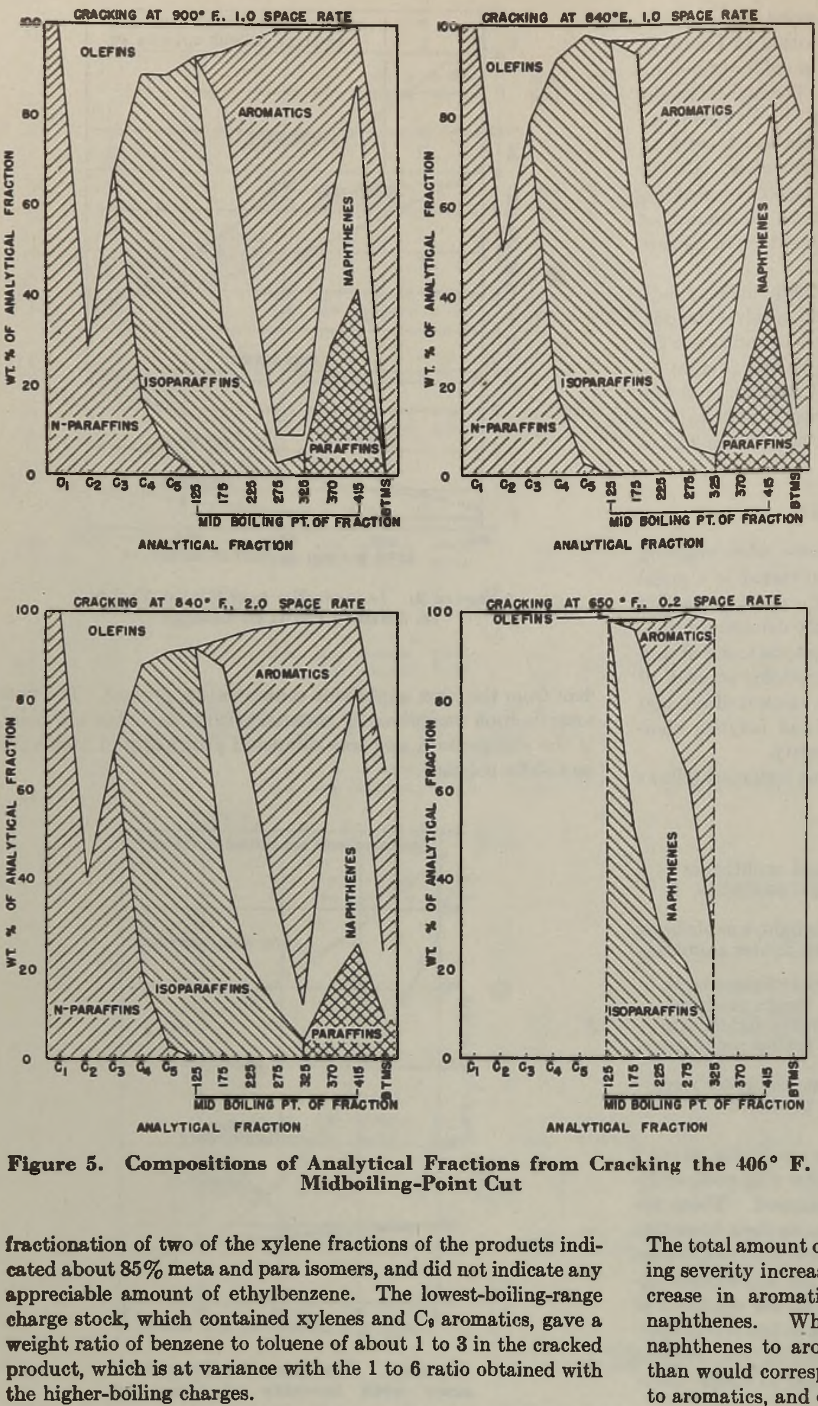


Figure 5. Compositions of Analytical Fractions from Cracking the 406° F. Midboiling-Point Cut

fractionation of two of the xylene fractions of the products indicated about 85% meta and para isomers, and did not indicate any appreciable amount of ethylbenzene. The lowest-boiling-range charge stock, which contained xylenes and $C_9$ aromatics, gave a weight ratio of benzene to toluene of about 1 to 3 in the cracked product, which is at variance with the 1 to 6 ratio obtained with the higher-boiling charges.

The distribution of paraffins between iso and normal compounds did not vary appreciably with charging stock or operating conditions, in so far as the paraffins were identical. The average weight ratios of iso to total paraffins were:

| | |
|---|---|
| Isobutane to total butanes | 0.807 |
| Isopentane to total pentanes | 0.935 |
| Isohexane to total hexanes | 0.973 |

Several of the lower-boiling analytical fractions were distilled in a small batch unit designed for a high degree of fractionation. The hexane fraction was found to be principally 2-methylpentane, with some 3-methylpentane and a small amount of 2,3-dimethylbutane. There was no indication of neopentane (2,2-dimethylpropane) or neohexane (2,2-dimethylbutane). Among the lower-boiling naphthenes no cyclopentane was found, but methylcyclopentane and cyclohexane were present.

## CONCLUSIONS

The composition of cracked products was found to vary regularly with the severity of cracking. Although cracking temperature was not chosen as an independent variable, it was varied along with the other conditions. In this way the relative contents of naphthenes (cycloparaffins) and aromatics were varied over a wide range. The greater the severity of cracking conditions (i.e., the greater the production of material boiling lower than the hexanes), the greater was the concentration of aromatics in the cracked distillate. It is indicated that maximum production of cracked naphthenes will occur at moderate cracking severity.

As the boiling range of the charging stock increases, the imposed cracking conditions are less severe, since the higher-boiling material is less refractory. In order to prevent "overcracking" and the destruction of desirable products, a lower partial pressure is imposed on the oil, either by lowering total pressure or by introducing steam. Also catalysts of suitable activity must be used. In this way the carbon deposited on the catalyst is controlled and limited to the desired figure of about 5.0% by weight at 1.0 space rate or 2.5% at 2.0 space rate. When cracking conditions are adjusted as described above, it is found that the production of light olefins increases with increase in boiling range. Correspondingly, the production of light isoparaffins decreases with increase in boiling range of the charge stock.

For the over-all cracking reaction, there is no evidence of the formation of ring compounds from chain material. The total amount of moles of ring was found to decrease as cracking severity increased, indicating a destruction of rings. The increase in aromatics was always less than the decrease in naphthenes. Whatever the mechanism of conversion of naphthenes to aromatics, the production of hydrogen is far less than would correspond to simple dehydrogenation of naphthenes to aromatics, and only approximately 40% of the naphthenes destroyed appear as aromatics.

In the lower-boiling aromatics ($C_9$ and lighter) produced, the concentration of benzene was always low, averaging 2.5% of the aromatics. The toluene production was fairly constant at about 14.5%. The ratio of xylenes to $C_9$ aromatics was 1 to 1, using a 406° F. midboiling-point charge stock, and decreased with the heavier charge cuts. Also this ratio was highest at the most severe cracking conditions. On the average, the weight ratio benzene:toluene:xylene was about 1:6:16, although it varied somewhat with conditions.

The ratio of iso to normal saturated hydrocarbons did not appear to vary appreciably with charging stock or operating conditions. As in previous work, neopentane (2,2-dimethylpropane) and neohexane (2,2-dimethylbutane) were substantially absent, as was cyclopentane.

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# PETROLEUM COKE

## Production of Compact Nonporous Coke

A. G. V. BERRY AND R. EDGEWORTH-JOHNSTONE

*Trinidad Leaseholds Ltd., Pointe-a-Pierre, Trinidad, B. W. I.*

**Experiments are described in which mixtures of pulverized petroleum coke and residuum or cracked asphalt were subjected to secondary coking. For the production of strong nonporous coke under conditions of rapid heating, two requirements were found necessary: (1) The volatile content of the primary coke should exceed 7%. (2) The calculated volatile content of the mixture of coke and binder should not exceed 22%. These findings are interpreted in the light of ideas in a previous paper (*1*).**

A PREVIOUS paper (*1*) reported a study of the formation of coke from asphaltic petroleum residues. It was found that the material always passes through an intumescent stage. This confers a more or less cellular structure on the resulting coke. When intumescence takes place under pressure, the cells are reduced in size, but they cannot be entirely eliminated. For this reason it is not ordinarily possible to produce nonporous coke from asphaltic residues in a single operation.

The usual procedure is to take a suitable petroleum coke, pulverize it, blend with 10–20% of asphalt or pitch, and recoke the mixture. This is the method by which smokeless briquets, electrodes, etc., are made. The mixture of coke and binder is pressed and molded before the second coking or "baking" process. Such products may be generally referred to as secondary coke, to distinguish them from the primary coke obtained by the direct carbonization of asphaltic residues.

The present paper describes laboratory experiments on the production of secondary cokes from mixtures of pulverized primary coke with residuum and cracked asphalt. These mixtures were not compressed before coking and were heated at a comparatively rapid rate. Any tendency towards intumescence and porosity could thus produce its maximum effect.

### PRODUCTION OF SECONDARY COKES

Samples of petroleum coke of known volatile content were pulverized to pass 40-mesh screen and mixed with various proportions of binder. Two different binders were used—a residuum from the cracking of topped crude and a cracked asphalt. The properties of these materials are given in Table I.

For each experiment 300 grams of the mixture of pulverized coke and binder were coked in the 3-inch cylindrical pot still described in the previous paper (*1*). In all cases the coke temperature was finally raised to 800° C. and maintained there for 2 hours.

Twenty-five experiments were made with cracked asphalt as binder, and twelve experiments with residuum. The secondary cokes produced were examined for strength and compactness. The results are shown in Tables II and III. Friability number was determined by a test described in the previous paper (*1*). Results are comparative only, a higher number denoting greater friability.

### SUMMARY OF RESULTS

1. Secondary cokes made from a primary coke of 7% volatile content were weak and friable when rapidly heated, and tended to be porous when heated more slowly.
2. Secondary cokes made from primary coke having a volatile content of 11% or more tended to be compact and nonporous, provided the total calculated volatile content of the mixture of coke and binder did not exceed about 22%.
3. Secondary cokes made from mixtures of primary coke and binder in which the calculated volatile content exceeded about 22% tended to be strong but porous.

The calculated volatile content of a mixture is taken as:

$$\frac{\left(\begin{array}{c}\%\text{ volatiles in binder }\times\\ \%\text{ binder in blend}\end{array}\right)+\left(\begin{array}{c}\%\text{ volatiles in coke }\times\\ \%\text{ coke in blend}\end{array}\right)}{100}$$

These results may be interpreted in the light of ideas put forward in the previous paper (*1*). It was there suggested that the coking of asphaltic residues is represented by the series:

$$\text{Asphalt}\longrightarrow\text{pitch}\longrightarrow\text{semipitch}\longrightarrow\text{asphaltic coke}\longrightarrow\text{carboid coke}$$

Semipitch has a volatile content of approximately 22–30% and intumesces when heated. Asphaltic coke has a volatile content of 7–22%, and carboid coke, of less than about 7%. Both the latter substances on heating lose volatile matter without intumescence. At precarbonization temperatures asphalt, pitch, semipitch, and asphaltic coke are more or less mutually soluble,

Table I. Properties of Binders

| | Residuum | Cracked Asphalt |
|---|---|---|
| Moisture | Nil | Trace |
| Organic volatile matter, % | 70.3 | 45.0 |
| Fixed carbon, % | 29.6 | 54.8 |
| Ash, % | 0.1 | 0.2 |
| Sulfur, % | ... | 1.8 |
| Sp. gr. at 60/60° F. | 1.060 | ... |
| Viscosity at 122° F., Saybolt Furol, sec. | 620 | ... |
| Ring and ball softening point, ° C. | ... | 125 |

TABLE II. SECONDARY COKING OF MIXTURES OF PULVERIZED COKE AND CRACKED ASPHALT

| Expt. No. | Volatile Content of Primary Coke[a], % | Compn. of Mixt., % | | Calcd. Volatile Content of Mixt.[a], % | Rate of Heating, ° C. per Min. | Yields, % | | Properties of Secondary Coke | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Coke | Asphalt | | | Distillate | Coke | Volatile content[a], % | Friability No. | Bulk density | General |
| I | 7 | 95 | 5 | 8.9 | 3.8 | 5.3 | 90.7 | 1.6 | Very friable | ... | Very friable and weak in structure |
| II | 7 | 90 | 10 | 10.8 | 4.7 | 6.7 | 87.0 | 2.1 | Same | ... | |
| III | 7 | 85 | 15 | 12.7 | 5.1 | 7.4 | 85.0 | 1.9 | Same | ... | |
| IV | 7 | 80 | 20 | 14.6 | 5.0[b] | 10.0 | 82.3 | 2.5 | Same | ... | |
| V | 7 | 75 | 25 | 16.5 | 5.0[b] | 11.0 | 81.7 | 2.4 | 19.4 | 0.566 | |
| VI | 7 | 77.5 | 22.5 | 15.6 | 6.2 | 12.3 | 81.3 | 1.8 | 60.1 | 0.454 | |
| VII | 7 | 77.5 | 22.5 | 15.6 | 2.7 | 9.0 | 78.0 | 2.2 | 41.5 | 0.501 | |
| VIII | 7 | 70 | 30 | 18.4 | 2.7 | 9.0 | 80.3 | 2.1 | 18.5 | 0.586 | Large No. of fine pores; very difficult to fracture |
| IX | 7 | 70 | 30 | 18.4 | 1.5 | 6.7 | 80.0 | 1.8 | 14.6 | 0.667 | Less porous than VIII and slightly stronger |
| X | 11 | 77.5 | 22.5 | 18.7 | 1.5 | 7.5 | 81.0 | 0.9 | 9.2 | 0.533 | ................ |
| XI | 11 | 72.5 | 27.5 | 20 3 | 1.5 | 10.3 | 80.0 | 1.1 | 3.5 | 0 667 | Less porous and more friable than XIV |
| XII | 11 | 75 | 25 | 19.5 | 1.5 | 10.7 | 80.7 | 1.0 | 4.6 | 0.673 | Less porous and more friable than XIV |
| XIII | 15 | 70 | 30 | 24.0 | 1.5 | 12.0 | 81.7 | 1.4 | 3.6 | 0.728 | Compact and granular |
| XIV | 15 | 75 | 25 | 22.5 | 1.5 | 11.0 | 76.0 | 1.5 | 3.0 | 0.732 | Compact and granular; stronger than XIII |
| XV | 15 | 80 | 20 | 21.0 | 1.5 | 10.7 | 79.0 | 1.7 | 10.6 | 0.574 | Less porous than XIV but not quite so strong |
| XVI | 15 | 77.5 | 22.5 | 21.7 | 1.5 | 11.0 | 76.7 | 1.7 | 2.8 | 0.715 | Very hard and strong in bulk |
| XVII | 15 | 77.5 | 22.5 | 21.7 | 3.0 | 10.0 | 76.0 | 1.8 | 4.6 | 0.537 | Compact structure but numerous cracks due to uneven contraction on cooling |
| XVIII | 15 | 77.5 | 22.5 | 21.7 | 6.6[b] | 12.3 | 75.3 | 1.7 | 5.6 | 0.537 | More porous than XVII; also more cracks and more friable |
| XIX | 15 | 77.5 | 22.5 | 21:7 | 0.5 | 4.3 | 79.7 | 1.4 | 5.0 | 0.590 | Porous but fairly strong |
| XX | 17.5 | 86 | 14 | 21.4 | 1.5 | 9.3 | 81.0 | 1.3 | 4.2 | 0.668 | Compact, very hard and strong; practically no pores |
| XXI | 17.5 | 80 | 20 | 23 | 1.5 | 9.3 | 76.3 | 0.62 | 6.1 | 0.670 | Porous and very friable |
| XXII | 17.5 | 90 | 10 | 20.35 | 1.5 | 6.7 | 79.7 | 0.83 | 6.5 | 0.581 | Compact and fairly strong, but not so strong as XX |
| XXIII | 20 | 90 | 10 | 22.5 | 1.5 | 7.7 | 82.6 | 1.6 | 1.5 | 0.675 | Porous and weak in bulk |
| XXIV | 20 | 95 | 5 | 21.2 | 1.5 | 8.3 | 81.0 | 1.3 | 2.5 | 0.683 | Very hard, compact, and strong |

[a] Organic volatile content.
[b] Approximate.

TABLE III. SECONDARY COKING OF MIXTURES OF PULVERIZED COKE AND RESIDUUM

(Rate of heating was 1.5° C. per minute until 800° C. was reached; the temperature was maintained at 800° C. for 2 hours)

| Expt. No. | Volatile Content of Primary Coke[a], % | Compn. of Mixt., % | | Calcd. Volatile Content of Mixt.[a], % | Yields, % | | Properties of Secondary Coke | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Coke | Residuum | | Distillate | Coke | Volatile content[a], % | Friability No. | Bulk density | General |
| XXV | 15 | 88 | 12 | 21.6 | 10.3 | 77.3 | 1.4 | 23 | 0.551 | Very powdery and weak |
| XXVI | 15 | 83 | 17 | 24.4 | 14.3 | 75.0 | 0.7 | 17 | 0.590 | Same |
| XXVII | 15 | 80 | 20 | 26.1 | 15.6 | 72.3 | 2.6 | 3.3 | 0.694 | Porous but fairly hard and strong |
| XXVIII | 15 | 78 | 22 | 27.2 | 17.3 | 70.3 | 1.3 | 8.4 | 0.657 | Residuum added to pulverized coke but not mixed; secondary coke varied considerably in quality; bottom portion fairly strong but porous |
| XXIX | 15 | 78 | 22 | 27.2 | 17.3 | 69.7 | 1.9 | 4.8 | 0.661 | Residuum and pulverized coke thoroughly mixed before heating; secondary coke better than XXVIII; strong, hard, and porous |
| XXX | 15 | 74 | 26 | 29.4 | 19.0 | 68.7 | 1.0 | 2.7 | 0.689 | Best coke obtained with primary coke of 15% volatile content; compact, strong and hard; see XXXIII |
| XXXI | 15 | 70 | 30 | 31.6 | 20.5 | 66.4 | 0.7 | 2.6 | 0.719 | More porous than XXX; no cooling cracks, but weaker than XXX although quite strong |
| XXXII | 15 | 67 | 33 | 33.4 | 23.1 | 64.9 | 0.9 | 3.5 | 0.715 | Cracks due to uneven contraction during cooling; weaker than XXXI but fairly strong |
| XXXIII | 20 | 92 | 8 | 24.0 | 10.3 | 76.0 | 0.3 | 4.8 | 0.632 | Best coke obtained from primary coke of 20% volatile content and similar to XXX; compact, hard, and strong |
| XXXIV | 20 | 90 | 10 | 25.0 | 11.0 | 75.7 | 0.4 | 4.3 | 0.631 | Coke fairly porous in center, sides compact; hard and strong |
| XXXV | 20 | 88 | 12 | 26.0 | 10.3 | 74.3 | 0.9 | 2.8 | 0.652 | Fewer but larger pores than XXXIV; hard and strong |
| XXXVI | 20 | 86 | 14 | 27.0 | 12.0 | 73.7 | 0.6 | 5.6 | 0.667 | Full of fine pores but fairly strong |

[a] Organic volatile content.

owing to their content of asphaltic matter. When a mixture of any two of them is heated, the mutually soluble constituents appear to diffuse into one another before coking begins. The mixture, therefore, carbonizes like a homogeneous material with intermediate properties. For example, a mixture of asphaltic coke and pitch or asphalt in which the calculated volatile content lies between 22 and 30% will intumesce on heating like a semipitch of similar volatile content. If, on the other hand, the calculated volatile content is below about 22%, the mixture behaves on heating like an asphaltic coke; i.e., it loses volatile matter without intumescence. Interdiffusion of asphaltic constituents between coke and binder creates a firm bond between them when the mixture is carbonized, and the baked product tends to be strong, compact, and nonporous.

Coke with a volatile content below about 7% is classified as carboid coke and is almost completely insoluble in organic solvents. When it is heated with pitch or asphalt, there is little or no interdiffusion and, hence, no firm bond between the primary coke and the binder. Unless the rate of heating is excessively slow, the binder itself intumesces and produces a secondary coke which is weak and friable.

Porosity results when volatile matter is evolved at such a rate that it cannot all be eliminated by diffusion through the mass of charge to the exposed surface. The excess volatile matter forms bubbles and may create fissures communicating with the surface of the mass. In mixtures which comply with condition 2 above, the volatile products are soluble in the asphaltic primary coke. Hence the whole mass of charge can take part in the elimination of volatile matter by diffusion, and this permits a rapid rate of heating without the formation of bubbles. In mixtures conforming to condition 1, the volatile products are insoluble in the primary coke, and diffusion can take place only through the residual binder which fills the interstices between the primary coke particles. The total diffusion path is greatly restricted as compared with condition 2, and an excessively low rate of heating is necessary to avoid porosity (lower than the slowest rate employed in the foregoing experiments).

Condition 1 corresponds to the procedure commercially employed in the manufacture of electrodes, as described by Boex (*2*) and Mantell (*3*). According to Mantell, the heating of a batch of electrodes occupies a period of 12–20 days.

Condition 3 again requires very slow heating to avoid porosity owing to the high percentage of volatile matter given off and to the fact that, even after an appreciable quantity has been evolved, the residual mass is still plastic.

The conditions of composition for obtaining a compact, nonporous secondary coke in the shortest possible baking time appear to be as follows: (1) The primary coke should be asphaltic coke with a volatile content well above 7%. (2) The calculated volatile content of the mixture of primary coke and binder should remain within the asphaltic coke range—i.e., below about 22%.

A few preliminary experiments have been made with laboratory samples molded under pressure before baking. The results tend to confirm the above interpretation. This investigation is at present suspended owing to pressure of more urgent work. The above results, and our conclusions regarding them, are published in the hope that they may be of interest to those engaged in the production of electrodes and other forms of commercial carbon.

## ACKNOWLEDGMENT

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# Treatment of Spent Pickling Liquors with Limestone and Lime

RICHARD D. HOAK, C. J. LEWIS, AND W. W. HODGE[1]
*Mellon Institute, Pittsburgh, Pa.*

**Where pickle liquor has been treated with lime and the sludge is oxidized, the stoichiometric quantity of lime is required; but where the sludge is discharged to a settling basin with a minimum of oxidation, approximately 95% of the theoretical amount of lime will afford complete treatment. Limestones vary widely in their rate of reaction with pickle liquor, and the rate depends upon particle size, chemical analysis, and a specific reactivity peculiar to a particular limestone. There is a critical particle size, falling between 200 and 325 mesh, and differing for different limestones, for optimum reaction between this material and pickle liquor. Where magnesium carbonate is present in limestone in excess of about 2%, the rate of reaction with pickle liquor is roughly inversely proportional to the percentage of this constituent. Dolomitic limestones are practically useless for pickle liquor treatment. The specific reactivity of limestones is an important factor which cannot be correlated and is determinable only by trial. The rate at which limestone removes iron from pickle liquor is a function of the rate at which ferrous iron oxidizes. Substantial economy in pickle liquor treatment can be realized by using pulverized high-calcium limestone, to neutralize free acid and precipitate part of the iron, and lime to complete the treatment. The commercial operation of a limestone-lime split treatment is described.**

THE removal of the oxide film from steel, preparatory to further processing, is usually accomplished by pickling the metal in a sulfuric acid bath. This treatment results in a waste liquor which is substantially an aqueous solution of ferrous sulfate and sulfuric acid. Many steel companies can dispose of this liquor only after treating it with lime to neutralize the free acid and precipitate the iron.

Lime treatment of waste pickle liquor is expensive; occasionally the cost of disposing of the spent liquor is as great as the cost of pickling. Colton (*2*) patented a process, described by Rentschler (*5*), for manufacturing a building material from the sludge produced in lime treatment. In many instances, however, no useful by-products can be recovered economically. Under these circumstances it is essential that the treating agent be utilized as effectively as possible. An appreciation of the importance of the several factors involved in the treatment of waste pickle liquor contributes to the most efficient operation of the process under a particular set of conditions.

Although a number of acids other than sulfuric (hydrochloric, nitric, hydrofluoric, phosphoric) are used in pickling steel, the quantities are small in comparison with sulfuric acid. Part of the experimental work reported in this paper was conducted with a straight sulfuric acid liquor, and part with a liquor containing small amounts of nitric and hydrofluoric acids in addition to the sulfuric acid which comprised the bulk of the pickling agent. The results of this investigation should be applicable to any of the waste liquors commonly resulting from pickling.

The authors (*4*) presented a scheme whereby determination of the basicity factor of an alkaline agent and the acid value of a waste liquor provides a rapid method for calculating the proportions of the two materials which should be combined to effect a desired result. This procedure has the advantage of quickly measuring the available basicity of an alkaline agent under the conditions of the treatment and eliminates speculation concern-

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[1] W. W. Hodge is an Advisory Fellow at Mellon Institute. His address is West Virginia University, Morgantown, W. Va.

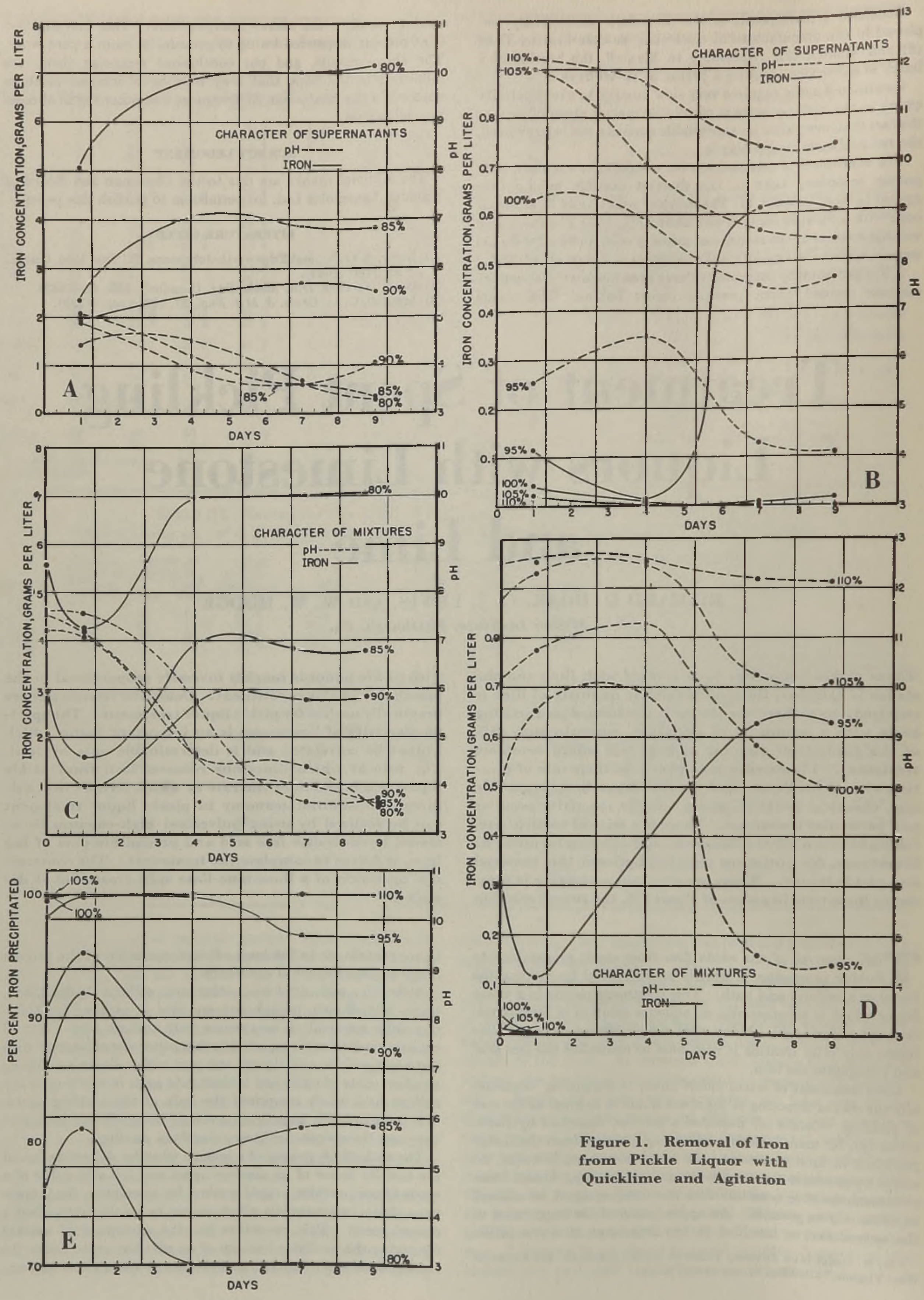

Figure 1. Removal of Iron from Pickle Liquor with Quicklime and Agitation

ing the applicability of basicities calculated from chemical analyses. The basicity factor–acid value relation was used as a basis for the experimental work to be presented because extensive investigation has demonstrated the reliability of the procedure.

### LIME TREATMENT WITH AGITATION

A group of experiments was conducted in which a sulfuric acid pickle liquor, containing 57.5 grams of iron per liter, was treated with several proportions of a high-calcium quicklime slurry; the amount of lime ranged from a substantial deficiency to a considerable excess of that required by the basicity factor–acid value relation. The mixtures were stirred with an electric mixer at intervals, and samples of the supernatants and filtrates from the sludges were analyzed for soluble iron.

**Procedure.** Seven 200-ml. portions of the pickle liquor (acid value, 146.3 grams sulfate per liter) were treated with quantities of high-calcium quicklime (basicity factor, 0.9292 gram calcium oxide per gram) ranging from 80 to 110% of that required for complete precipitation of iron according to the basicity factor–acid value relation. The lime was slaked in warm water in a proportion of 1 to 5 and added to the pickle liquors in liter beakers. The mixtures were stirred 5 minutes, pH was determined, and samples were taken for analysis. They were then stirred 15 minutes and allowed to stand overnight at room temperature. The next day the pH values of the supernatants were determined electrometrically, 20-ml. samples were filtered, and the filtrates were analyzed for iron. The mixtures were then stirred for 15 minutes, the pH values determined, 20-ml. samples filtered, and the filtrates analyzed for iron. The sludge cakes were discarded. This procedure was repeated on the second, fifth, eighth, and tenth days, except that the mixtures were stirred for one hour on the eighth and tenth days before sludge samples were withdrawn for analysis.

The results of these experiments are given graphically in Figure 1. The curves show that, where a deficiency of lime is used, the concentration of soluble iron first decreases; then as oxidation proceeds and the pH falls, it increases to some equilibrium value. This effect is more pronounced in the sludges than in the supernatants because of the presence of lime particles which react slowly over several days in the former. The phenomenon is illustrated clearly in Figure 1*E* where the percentage of iron precipitated in the systems as a whole is plotted against time.

It is significant that, where 95% of the required amount of lime was used, a phenolphthalein end point could be obtained 4 days after treatment. If an operator was using phenolphthalein as an indicator of complete treatment, he would obtain an end point when insufficient lime had been added. This reaction could be observed transitorially where greater deficiencies of lime were used and mixing was inadequate. Where the basicity factor–acid value relation is employed, the proportions of lime and pickle liquor can be calculated quickly, and no dependence need be placed on indicators which may yield misleading results.

Attention is directed to the 100% curves in Figures 1*B* and *D*, which indicate that the supernatant from a pickle liquor treated with the theoretical quantity of lime may contain a trace of iron after 10 days, but the filtrate from a sample of the sludge will contain none. This probably results from the entrapment of lime particles in the sludge where they cannot react readily. Metal ions are distributed relatively uniformly throughout such a sludge, and if the mixture is agitated and allowed to settle, those ions which were not in contact with the entrapped lime particles appear in the supernatant. A sufficiently long mixing period will result in complete precipitation of the iron where the requisite amount of lime is used.

### LIME TREATMENT WITH QUIESCENT SETTLING

In the experiments described in the preceding section approximate equilibrium was attained much more rapidly than would ordinarily be possible in practice. The experiments were performed in this manner to provide data on the tendency of iron to redissolve after precipitation had apparently been complete. The data indicate the quality of the supernatant and the sludge seepage to be expected from a lagoon containing lime-treated pickle liquor where oxidation was relatively complete.

Where pickle liquor is treated with lime, it is usual practice to discharge the slurry to a lagoon after a brief mixing period. Under such conditions the iron dissolved in the supernatant oxidizes fairly rapidly, but oxidation of iron in the sludge occurs slowly, depending on the rate at which oxygen from the air can diffuse through the supernatant liquor. Indeed, the sludge in a lagoon might not oxidize completely in several years.

The use of the basicity factor–acid value relation is based on the fact that treatment of pickle liquor with lime is equivalent to supplying enough calcium ion to combine with all of the sulfate ion (or other acid ions) present. Oxidation of ferrous iron should result in a decrease in pH sufficient to permit re-solution of iron only where insufficient lime is present in the stoichiometric proportion to satisfy all anions. This is illustrated in the reactions

$$2FeSO_4 + 2Ca(OH)_2 = 2Fe(OH)_2 + 2CaSO_4 \quad (1)$$

$$2Fe(OH)_2 + H_2O + {}^1/_2O_2 = 2Fe(OH)_3 \quad (2)$$

$$\text{Adding: } 2FeSO_4 + 2Ca(OH)_2 + H_2O + {}^1/_2O_2 = 2Fe(OH)_3 + 2CaSO_4 \quad (3)$$

which show that a molecule of ferrous sulfate, whether it is precipitated as in reaction 1 or later oxidized as in reaction 2, requires but one molecule of lime as shown in the summation Equation 3.

When ferrous salts react (*1*) with an alkaline agent, the precipitate which forms is a basic salt rather than a simple hydroxide, and the more rapidly the alkali is added, the less basic is the precipitate. The sulfate ion forms basic salts which are more stable than those of other common anions. Ferric salts have an even more pronounced tendency than ferrous salts to form basic compounds, and the rate of oxidation of ferrous salts increases rapidly with the increase in the pH of the liquor when lime is added to it. This phenomenon has the effect of removing from solution anions which would otherwise combine with calcium ions, leaving an excess of calcium hydroxide over the stoichiometric requirement of the liquor.

Under these conditions it appeared possible to treat pickle liquor satisfactorily with somewhat less lime than the acid value of the liquor would indicate. The point was investigated by treating a sulfuric acid pickle liquor containing 55.75 grams iron per liter, plus small quantities of nitric and hydrofluoric acids, in a manner which would approximate the practical operation of a lime treatment plant, with 90, 95, and 100% of the lime necessary to satisfy the basicity factor–acid value relation.

**Procedure.** Three 25-gallon portions of a waste pickle liquor (acid value, 202.6 grams sulfate per liter) were treated in 55-gallon steel drums with 90, 95, and 100% of high-calcium lime (basicity factor, 0.9565 gram calcium oxide per gram) which had been slaked with water in the proportion of 1:4. The lime slurry was added before the heat of slaking had been dissipated, and the liquors were stirred with an electric mixer during the lime addition. The mixtures were then stirred for 20 minutes longer. The slurries resulting from this procedure were quite heavy, and to promote better mixing about 6 gallons of water were added during the mixing period in each case. The mixtures were allowed to stand undisturbed, except for the removal of samples, until the runs were completed. Samples of sludges and supernatants were taken daily for 10 days, then every other day for about 10 days, and finally at increasing intervals. Representative samples of the sludges were taken by removing a cylinder of sludge in a glass tube inserted to the bottom of each drum. The pH of each sample was determined electrometrically, and filtrates from the samples were analyzed for iron.

The results of these experiments are shown graphically in Figure 2. Duplicates of the 90 and 95% runs were made; the results satisfactorily checked those shown for these two mixtures in Figure 2. The figure shows that, when the quantity of lime required by the basicity factor–acid value relation is thoroughly mixed with pickle liquor, the iron is quickly and completely precipitated. The single point showing iron in the sludge after 5-day settling probably resulted from striking with the sampling tube a small region in the sludge where mixing had been incomplete.

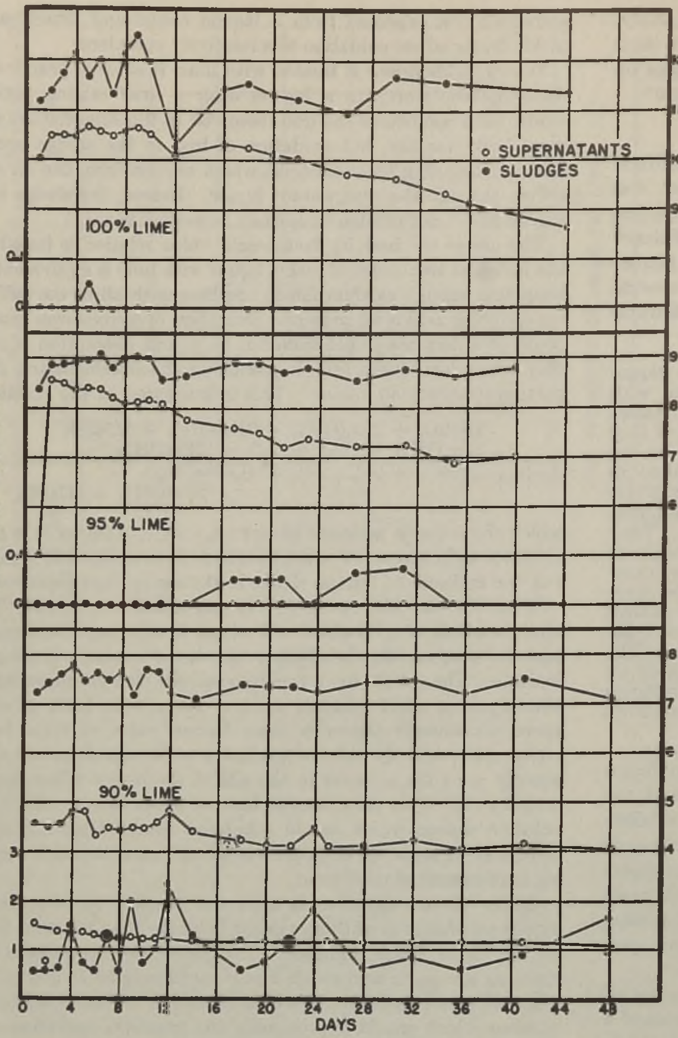

Figure 2. Removal of Iron from Pickle Liquor with Quicklime and Quiescent Settling

It is probable that the pH of the supernatant in this and in the 95% system was affected by solution of carbon dioxide from the air.

Where only 95% of the required lime is used, Figure 2 indicates that satisfactory results would usually be obtained if the sludge was allowed to settle in a lagoon according to general practice. If the sludge is agitated, however, to permit oxidation to proceed, the pH of the sludge falls rapidly and iron appears in solution. Figure 3 illustrates the data obtained when a portion of the 95% sludge, after having settled for 44 days, was agitated with an electric mixer.

It is clear from Figure 2 that, when as little as 90% of the required amount of lime is used, the iron cannot be completely precipitated, either in sludge or supernatant, with quiescent settling.

## PULVERIZED LIMESTONE TREATMENT

Lime treatment of pickle liquor has been common for many years, but the development of processes for using limestone for this purpose has received scant attention. Limestone would appear to be a logical alkaline material for pickle liquor treatment because of its wide geographical distribution and relatively low price. It has been used occasionally, usually by permitting the liquor to percolate through beds of lump limestone, but the results have usually been unsatisfactory. Where a sulfuric acid pickle liquor reacts with lump limestone, the deposit of a relatively impervious layer of calcium sulfate on the stone prevents the utilization of more than a fraction of its alkalinity.

Pulverized limestone can be utilized much more effectively than lump or crushed stone because the fine particles tend to react more or less completely. Such material will quickly neutralize free acid and precipitate ferric iron in pickle liquor, but will not precipitate ferrous iron completely, even if it is reduced to extreme fineness, because it cannot produce a sufficiently high pH. But the rate of oxidation of ferrous sulfate increases rapidly with an increase of the pH of the solution; where oxygen can be supplied by aeration or otherwise, many pulverized limestones will precipitate all of the iron from an aqueous solution of a ferrous salt if the oxidation of the iron is allowed to go to substantial completion.

Pulverized limestones vary widely in their rate of reaction with pickle liquor. Reaction rates are governed by chemical analysis, fineness, and a specific reactivity, peculiar to a particular limestone, which cannot easily be evaluated except by trial. The experimental work which follows indicates that the magnesium carbonate content of a limestone exerts a profound effect on its rate of reaction. Other factors, such as the geologic history of the stone, its crystal structure, the kind and amount of impurities, probably affect its reactivity in some degree, but its rate of reaction appears to be approximately inversely proportional to the quantity of magnesium carbonate it contains (above about 2%). Ferrari and Sessa (*3*) found that calcite and synthetic calcium carbonate each reacted about one hundred and fifty times as rapidly with an acid solution as dolomite. They pointed out that the velocity of solution of various compounds diminishes rapidly with diminution of the radii of their cations. Voznesenskiĭ, Evlonova, and Suvorova (*6*) found that dolomite reacted rapidly with strong acids and that the dolomite could be utilized almost completely; but the acidity of the liquor was reduced only to 0.5–0.6% sulfuric acid.

TABLE I. SCREEN ANALYSIS OF PULVERIZED LIMESTONES

| Limestone | +65 | −65<br>+100 | −100<br>+200 | −200<br>+325 | −325 |
|---|---|---|---|---|---|
| A | 0.0% | 1.5% | 10.0% | 28.0% | 60.4% |
| B | 2.1 | 5.9 | 20.4 | 37.9 | 31.2 |
| C | 0.0 | 0.4 | 0.8 | 85.0 | 13.0 |
| D | 1.2 | 3.8 | 10.3 | 41.9 | 40.7 |
| E | 0.2 | 0.7 | 1.9 | 15.0 | 81.7 |
| F | 0.2 | 1.0 | 12.8 | 33.6 | 51.7 |
| G | 0.2 | 1.6 | 11.7 | 83.5 | 2.5 |
| H | 0.0 | 0.3 | 7.0 | 33.5 | 58.0 |
| I | 0.0 | 0.0 | 4.0 | 21.5 | 74.2 |

TABLE II. ANALYSIS AND BASICITY FACTORS OF PULVERIZED LIMESTONES

| Limestone | Loss at 150 ° C., % | Acid Insol., % | $R_2O_3$, % | $CaCO_3$, % | $MgCO_3$, % | Basicity Factor |  |  |
|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  | Calcd. | HCl | $H_2SO_4$ |
| A | 0.17 | 0.73 | 1.09 | 93.90 | 2.26 | 0.5416 | 0.5596 | 0.5543 |
| B | 0.11 | 0.35 | 0.49 | 54.28 | 44.31 | 0.6006 | 0.6015 | 0.6004 |
| C | 0.00 | 4.20 | 0.49 | 95.33 | 0.75 | 0.5417 | 0.5382 | 0.5369 |
| D | 0.10 | 5.60 | 1.31 | 87.35 | 1.05 | 0.4974 | 0.4971 | 0.4982 |
| E | 0.06 | 0.94 | 0.29 | 96.97 | 0.79 | 0.5490 | 0.5601 | 0.5540 |
| F | 0.13 | 1.64 | 0.38 | 86.97 | 10.89 | 0.5594 | 0.5635 | 0.5612 |
| G | 0.10 | 2.21 | 0.50 | 96.91 | 1.17 | 0.5520 | 0.5596 | 0.5468 |
| H | 0.08 | 2.35 | 0.44 | 95.10 | 1.50 | 0.5458 | 0.5406 | 0.5465 |
| I | 0.08 | 3.72 | 0.68 | 51.84 | 42.62 | 0.5754 | 0.5684 | 0.5757 |

Nine pulverized limestones were investigated in the experimental evaluation of such products for pickle liquor treatment. The samples were chosen to represent not only the major producing centers, which are widely distributed geographically, but also the most important geological deposits. Table I gives the screen analyses of the eight commercial pulverized limestones studied and one (I) which was ground in the laboratory.

The fractions of these samples passing a 325 mesh U. S. Standard screen were analyzed chemically, ultimate basicity factors were determined with hydrochloric and with sulfuric acid, and basicity factors were calculated from the chemical analyses. The data appear in Table II. The −325 mesh fractions of the samples were analyzed to ensure that ultimate basicities could be obtained with sulfuric acid in a 30-minute boiling period so that these basicities could be compared with those calculated from the chemical analysis of these samples.

There is a critical particle size which varies with different types of limestone; among the limestones studied, this size is finer than 200 mesh. It is important to recognize, however, that fineness and basicity are interdependent factors. For practical purposes the rate of reaction of limestones increases little when particle sizes finer than the critical are used. This is important because a material much finer than 200 mesh contributes little to the efficiency of the process, and grinding costs increase rapidly as finer and finer screen sizes are specified. A pulverized limestone of which 80 to 85% passes 200 mesh would be satisfactory, other things being equal, and in general ordinary pulverized limestones will meet such a specification. In fact, a large proportion of the −200 mesh material will also be −325 mesh, and it is unnecessary to pay the higher price for a superfine material.

Table II illustrates the close agreement between ultimate basicity factors and those calculated from the chemical analysis. However, only ultimate basicity factors agree with those calculated from analysis. Where the conditions of treatment require that a basicity factor lower than the ultimate be used, the error might be substantial if the factor was calculated from an analysis. Table III presents sulfuric acid basicity factors determined on the eight pulverized limestones, as received.

The ultimate basicity factors of Table III do not agree with those of Table II because the latter were determined on a whole sample, the former on a −325 mesh fraction. As impurities, particularly silica, tend to concentrate in the finer fractions, the higher the silica in the original sample, the greater will be the effect on the basicity factor of a fine fraction. Any attempt to explain the minor variations in Table III would be speculative. The figures represent averages of several determinations in each case, and they show that basicity factors should be run on as large a sample as can be handled conveniently. Figure 4 shows microphotographs taken from representative fields on slides of samples of the eight limestones as received.

The data reveal considerable physical and chemical differences between the limestone samples. Portions were stirred with a pickle liquor to study differences in their rates of reaction.

PROCEDURE. One liter of pickle liquor (acid value 209.3 grams sulfate, 63.78 grams iron) was placed in a 4-liter beaker equipped with an electric mixer. The liquor was diluted with an equal volume of water to avoid an inconveniently high viscosity and to provide an ample volume for removal of samples. A quantity of pulverized limestone (as received) equivalent to the acid value, based upon a one-hour sulfuric acid basicity factor, was added. Samples of the slurries were withdrawn at intervals, pH values determined electrometrically, and filtrates analyzed for iron. The mixtures were stirred constantly from beginning to end of a run, except for the least reactive limestones where it was necessary for the mixtures to stand overnight. A negligible change occurred where such mixtures stood without agitation.

The data from these experiments are presented graphically in Figure 5. Samples of the same pickle liquor, which contained a small amount of nitric and hydrofluoric acids in addition to the sulfuric acid, were used for all the curves except F2 and $MgCO_3$. The oxidative effect of the nitric acid is shown by the initial difference in iron removal when limestone F reacted with the two liquors. Comparison of these curves with the analyses of Table II shows that there is rough inverse proportion between the reactivity of a limestone and its magnesium carbonate content.

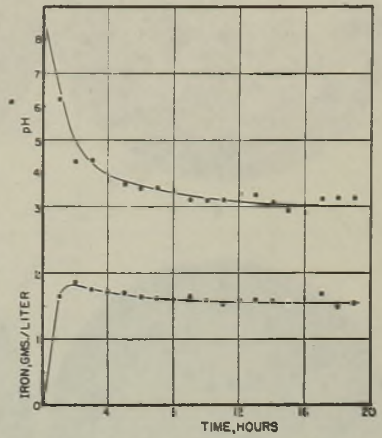

Figure 3. Removal of Iron from Pickle Liquor with Quicklime and Agitation of 95% System, after 44-Day Quiescent Settling

Apparently magnesium carbonate contents below about 2% do not have a marked effect on reactivity, but above such a point the effect is striking. Although there are many other factors which influence reactivity, it is a significant fact that the low reactivity of magnesian limestones makes them relatively useless for pickle liquor treatment. The curve for magnesium carbonate indicates that the physical combination of the magnesium carbonate in limestone affects the reactivity of the stone. The magnesium carbonate used in this experiment was U.S.P., and its specification permits the sale of hydrated basic carbonate as well as hydrated normal carbonate under this quality. Anhydrous normal magnesium carbonate would have a basicity factor of 0.665 gram calcium oxide per gram; the U.S.P. sample used had a basicity factor of 0.581. Curve B represents a pure dolomite, and the dotted line indicates that at that point a 100% excess of the limestone was added. Curve I represents a stone, believed to be not a true dolomite, in which the calcium and magnesium carbonates are present in the approximate molecular proportions of dolomite. These experimental curves illustrate the effect of the specific reactivity of a given limestone. For example, comparing limestones C and G, on the basis of fineness and basicity factor the former would appear to be the more desirable agent whereas in practice the latter is considerably more effective.

A one-hour basicity factor was arbitrarily chosen for these comparisons because it represents a reasonable mixing period in practice. Where pickle liquor is treated with quicklime, the ba-

TABLE III. BASICITY FACTORS OF PULVERIZED LIMESTONES

| Limestone | Basicity Factor at Boiling Time of: 30 min. | 60 min. | 90 min. | 120 min. | 150 min. | 180 min. | Ultimate |
|---|---|---|---|---|---|---|---|
| A | 0.5110 | 0.5155 | 0.5217 | 0.5323 | 0.5402 | 0.5435 | 0.5578 |
| B | 0.5755 | 0.5813 | 0.5908 | 0.5915 | 0.5917 | 0.5924 | 0.6016 |
| C | 0.5451 | 0.5476 | 0.5483 | 0.5471 | 0.5498 | 0.5480 | 0.5483 |
| D | 0.4600 | 0.4627 | 0.4792 | 0.4823 | 0.4917 | 0.4988 | 0.5018 |
| E | 0.5374 | 0.5444 | 0.5487 | 0.5504 | 0.5548 | 0.5558 | 0.5579 |
| F | 0.5129 | 0.5177 | 0.5315 | 0.5343 | 0.5443 | 0.5588 | 0.5595 |
| G | 0.5020 | 0.5145 | 0.5315 | 0.5328 | 0.5443 | 0.5453 | 0.5529 |
| H | 0.5136 | 0.5298 | 0.5332 | 0.5399 | 0.5339 | 0.5365 | 0.5378 |

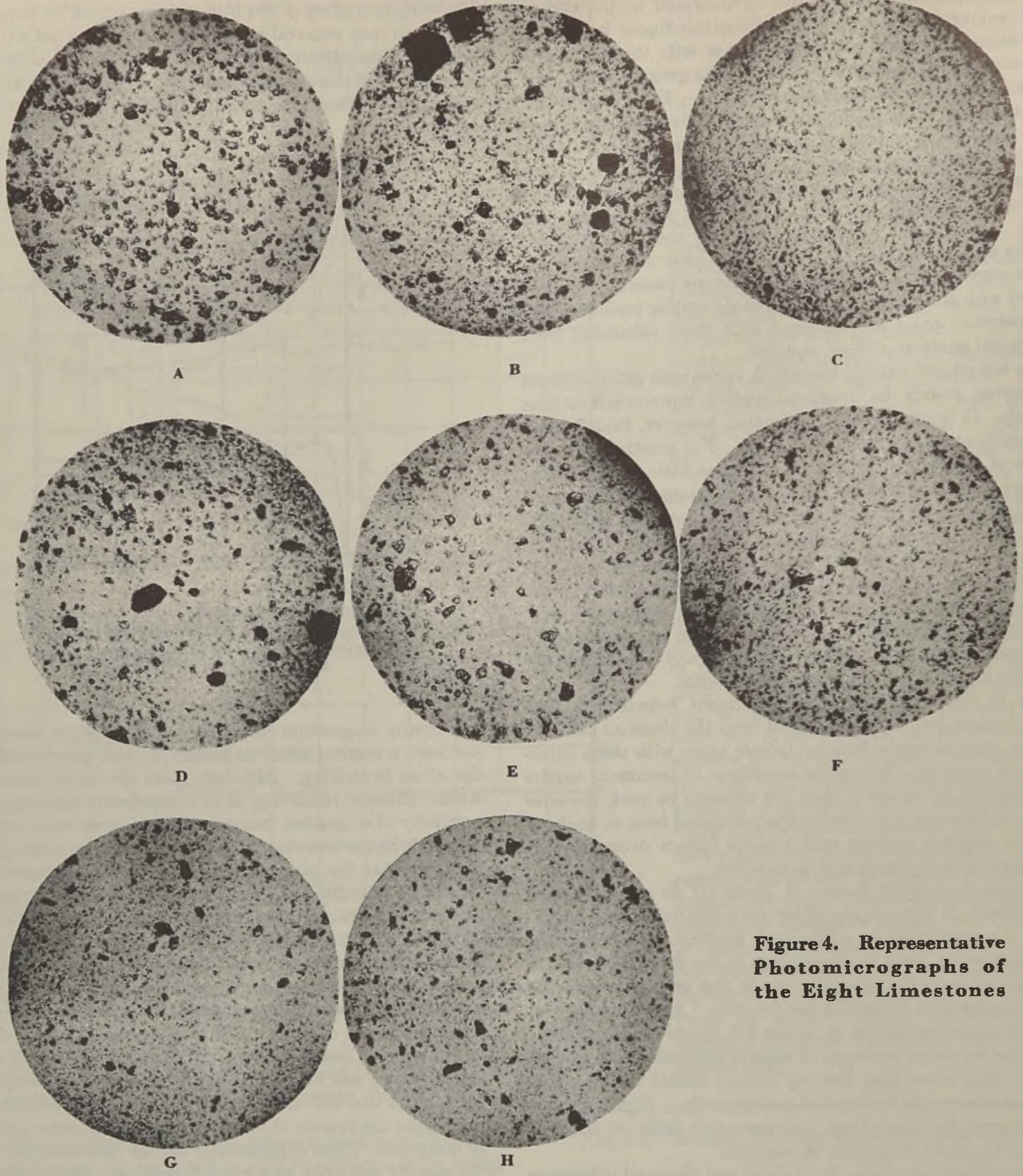

Figure 4. Representative Photomicrographs of the Eight Limestones

sicity factor–acid value relation affords a convenient and accurate control; where pulverized limestones are used, basicity factors serve as approximations for high-calcium limestones but are relatively useless for magnesium stones.

### LIMESTONE–LIME SPLIT TREATMENT

The findings presented in the preceding sections suggested that economies in pickle liquor treatment might be realized by using pulverized limestone to neutralize the free acid and precipitate part of the iron, and quicklime to complete the treatment. Laboratory studies showed that such a process was feasible and, if operated under the most favorable conditions, that the savings from its use would be substantial.

A steel company cooperated in the investigation by permitting the authors to make plant-scale runs of this process in its pickle liquor treatment equipment. A series of experimental runs was made in which 800-gallon batches of pickle liquor were treated in the same plant which was currently using quicklime to provide complete treatment. The trial runs successfully demonstrated the practicability of the process and the company, after a 30-day test period with its own operators, adopted the split treatment because of its economy over the use of quicklime alone.

In the operation of the process pulverized limestone is added while the liquor is agitated rapidly, until the sludge turns light yellow. As all pickle liquors contain more or less ferric iron, the addition of limestone until trivalent iron precipitates is an indication[1] that all of the free acid has been neutralized. Agitation of the slurry is continued without further additions until examination of a sample dipped out with a paddle indicates that evolution of gas has practically ceased. It is important that the bulk

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[1] This is a sharp end point which is easily recognized if sufficient ferric iron is present in the liquor. Where a trial shows that the liquor contains too little ferric iron, the addition of oxidized sludge to the reaction vessel will provide enough. Because treatment tanks are not pumped dry, each batch after the first should contain ample ferric iron.

of the entrained carbon dioxide be expelled to prevent its subsequent reaction with the lime. Only 5–8 minutes are required to ensure the elimination of most of the gas. Milk of lime is then run in from the lime-slaking tank until a pink color is obtained with phenolphthalein on a spot plate, and the treatment is complete. Although phenolphthalein first turns pink at a pH of about 8.3 and it is desired to finish the treatment at pH 9 or higher, usually enough time will elapse between taking the test and turning off the lime feed for the desired result to be attained.

Evolution of carbon dioxide in the limestone treatment causes no difficulty. In the plant operation, limestone is added as rapidly as possible (fourteen 80-pound bags in 3 minutes) to a reaction tank with a freeboard of less than 4 feet, and it does not froth over. Installation of an exhaust fan is desirable for winter operation to keep the concentration of carbon dioxide in the room at a low level; such a fan also removes limestone dust and acid mist and thus permits the ferric end point to be seen clearly. The time required to treat a batch by this process is no greater than when lime alone is used; installation of a bin for feeding bulk limestone would reduce the time somewhat.

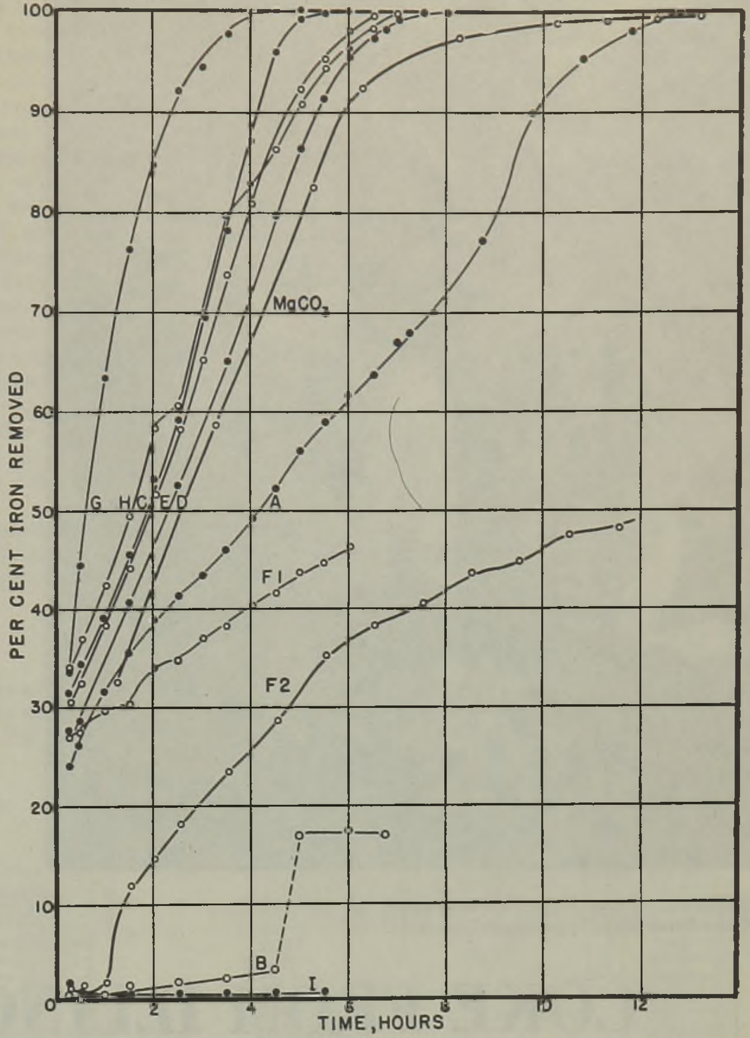

Figure 5. Rate of Removal of Iron from Pickle Liquor with Pulverized Limestone

## CONCLUSIONS

Although a quicklime slurry is commonly used for the purpose, the cost of pickle liquor treatment can be substantially reduced in many areas under favorable conditions by employing a combination of limestone and lime. The economy which can be realized by substituting the limestone–lime split treatment for treatment with lime alone depends largely on the cost of pulverized limestone. In some areas the prices of crude bulk quicklime and pulverized limestone will be equivalent in terms of calcium oxide, and there will be no great advantage in using limestone. Frequently, however, pulverized limestone can be obtained locally at a considerable saving; it can sometimes be purchased for 1 to 2 dollars per ton. Where limestone can be bought at a lower cost than the equivalent amount of lime, adoption of the split treatment results in savings.

Where the treating equipment is of sufficient size and limestone can be purchased at a satisfactory price, the savings from the split treatment can be increased by taking advantage of the ability of limestone to precipitate a greater proportion of the iron as the stirring period is increased. In this way as much of the treatment as possible would be accomplished with the cheaper material. Indeed, in a mill which produces a relatively small volume of liquor, treatment with a high-calcium limestone alone may be practicable.

In evaluating the relative economics of treating pickle liquor with lime alone, with the split treatment, or with limestone alone, it should be kept in mind that bulk lime must be stored in an airtight bin to prevent recarbonation and that lime is a skin irritant; pulverized limestone does not have these disadvantages. The installation of bulk storage and dry-feeding equipment for both materials will reduce the treatment cost by saving the bagging charge; such saving will range from 10 to 20% of the cost of the bagged product. Also, where sludge storage space is limited, it is important to recognize that the sludge produced by a limestone treatment has a smaller volume than that produced by lime.

## ACKNOWLEDGMENT

Acknowledgment is due to the American Iron and Steel Institute for permission to present this paper; to the many limestone companies which contributed the samples from which those studied were selected; to the Sharon Steel Corporation for permission to make plant scale tests at its works; and to Bernice Klein, Fellowship Assistant, who made many analyses for this investigation.

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Figure 1. Discharging and Quenching Coke from Slot-Type Experimental Oven

**Midwestern by-product coke ovens require annually millions of tons of high-volatile bituminous coals which are shipped from the Appalachian coal fields in West Virginia, Pennsylvania, and eastern Kentucky. Illinois has larger reserves of high-volatile bituminous coals than any other state east of the Rockies. Though the Appalachian coals are principally of higher rank than the midwestern, the reserves of these high-rank coals are being depleted rapidly. Because of this and the present critical transportation problem, the Illinois State Geological Survey, aided by the Office of Production Research and Development, War Production Board, initiated a research program to study the problem of substituting midwestern coals for a portion of the eastern high-volatile coals now being carbonized in midwestern coke ovens. Previous commercial and semicommercial experience has shown that metallurgical coke can be made from certain Illinois coals. The research program includes the design, construction, and operation of a pilot-size coke oven to duplicate carbonizing conditions in commercial slot-type ovens. A slot-type pilot-size coke oven of 500-pound coal capacity, electrically heated to ensure accurate temperature control, is described. The yields and properties of the coke and by-products recovered from this small experimental oven correlate closely with those obtained by carbonizing the same coals in commercial ovens. Thus, this oven is a reliable guide for commercial operations.**

# COKE FROM ILLINOIS COALS

## An Experimental Slot-Type Oven

FRANK H. REED, HAROLD W. JACKMAN, AND P. W. HENLINE

*State Geological Survey, Urbana, Ill.*

MIDWESTERN by-product coke ovens use annually millions of tons of high-volatile bituminous coals which are shipped from the Appalachian coal fields in West Virginia, Pennsylvania, and eastern Kentucky. Illinois has larger reserves of high-volatile bituminous coal than any state east of the Rocky Mountains; only Colorado exceeds Illinois in reserves. Although the Appalachian coals are principally of higher rank than the midwestern coals, the reserves of these high-rank Appalachian coals are being depleted rapidly.

This growing scarcity of the best Appalachian coals and the critical transportation problem now confronting the nation, prompted the Illinois State Geological Survey, aided by the Office of Production Research and Development of WPB, to begin a research program to study the possibilities of substituting midwestern coals for a portion of the eastern high-volatile coals now being carbonized in the Chicago and St. Louis districts. Freight rates to the Gary–East Chicago–Chicago district by rail favor the southern Illinois coals over the Appalachian coals by more than one dollar per ton. When a combination of rail haul from the Appalachian fields to a Lake Erie port and then lake barge to the Chicago district is used, the southern Illinois coal can still be delivered with a saving in freight of 50 cents per ton. It costs over 2 dollars per ton more to deliver Appalachian coals by rail to the St. Louis district than to deliver southern Illinois coals to the same point.

Illinois coals contain more moisture than do the Appalachian coals, however, and a correspondingly lower amount of fixed carbon on the as-received basis. Thus a lower yield of coke per ton of coal is obtained from the Illinois coals. Previous commercial and semicommercial experience has shown that "a fairly satisfactory grade of metallurgical coke" (*4*) can be made from coal of certain southern Illinois mines. Undoubtedly the methods of coal preparation and the resulting quality of coal shipped from these mines are better today than they were during the last war, or during the period from 1921 to 1934 when Franklin County, Ill., coal was used in the Roberts ovens at Granite City, Ill.

The comparison of costs to be obtained by coking Appalachian coals alone or in combination with Illinois coals in any given plant can be determined only by commercial operation over an extended period of time. The suitability of the coke for blast furnace operation, the yield of coke from the coal, and the amount and evaluation of the by-products are among the principal items which must be considered, along with freight rates, cost, and uniformity of coal supply, to determine the over-all economic picture. However, the cost of experimentation with various blends of coal in commercial coke ovens is not only exceedingly high, but it also interferes with regular production. Consequently, only a minimum of such experimentation is carried out.

The first objective of the present research program was, therefore, the design and construction of a small-scale slot-type coke oven in which blends of coals could be carbonized under conditions approximating those obtained in commercial ovens closely enough to produce cokes with physical and chemical properties directly comparable to those of cokes produced from the same blends in commercial ovens. Representative data selected from the first fifty runs are shown in Table I to indicate that this objective has been attained.

This paper gives briefly the construction and operation of the experimental slot-type oven, shows the duplicability of operating results, and compares results obtained with this experimental oven and with commercial slot-type ovens.

## DESIGN OF OVEN

The primary objective in design of the experimental slot-type oven was to construct a unit which would duplicate essentially a small section of a commercial oven, and in which the process of coking coal would be controlled rigidly. This was based on the assumption that the coking process is a complex chemical reaction. Thus, duplication of operating conditions from one run to another with identical blends of coal should produce batches of coke with identical physical and chemical properties. In practice "identical blends" are not obtainable, but blends with similar average physical and chemical properties can be obtained; therefore the cokes produced from such blends should have similar physical and chemical properties.

Only in the width of the oven was an attempt made to duplicate any size dimension of a commercial oven. The average width of most commercial slot-type ovens ranges from 13 to 21 inches. The average width of the experimental oven is slightly above the lower limit of this range. Thus, the oven was designed so that it could be operated to give the same heat penetration (average width of oven in inches divided by coking time in hours) and final temperature as obtained in commercial practice.

Figure 1 shows the slot-type experimental oven being discharged and the coke being quenched. The uniform oven wall temperature up to the top of the charge and the slightly cooler space above for gas collection are apparent. Also visible are the coal-charging hole, the door with opening for leveling bar, and other details of oven construction, including buckstays and angle-iron supports in the side walls.

Figure 2 is a diagram showing cross-sectional views from the front and side of the oven. As in all slot-type coke ovens, heat is applied from flues placed on both sides of the oven chamber, 1. The inside of the oven chamber was designed to taper in width from 13.25 inches at the back to 13.75 inches at the front. On account of irregularities in the shapes received, the oven as con-

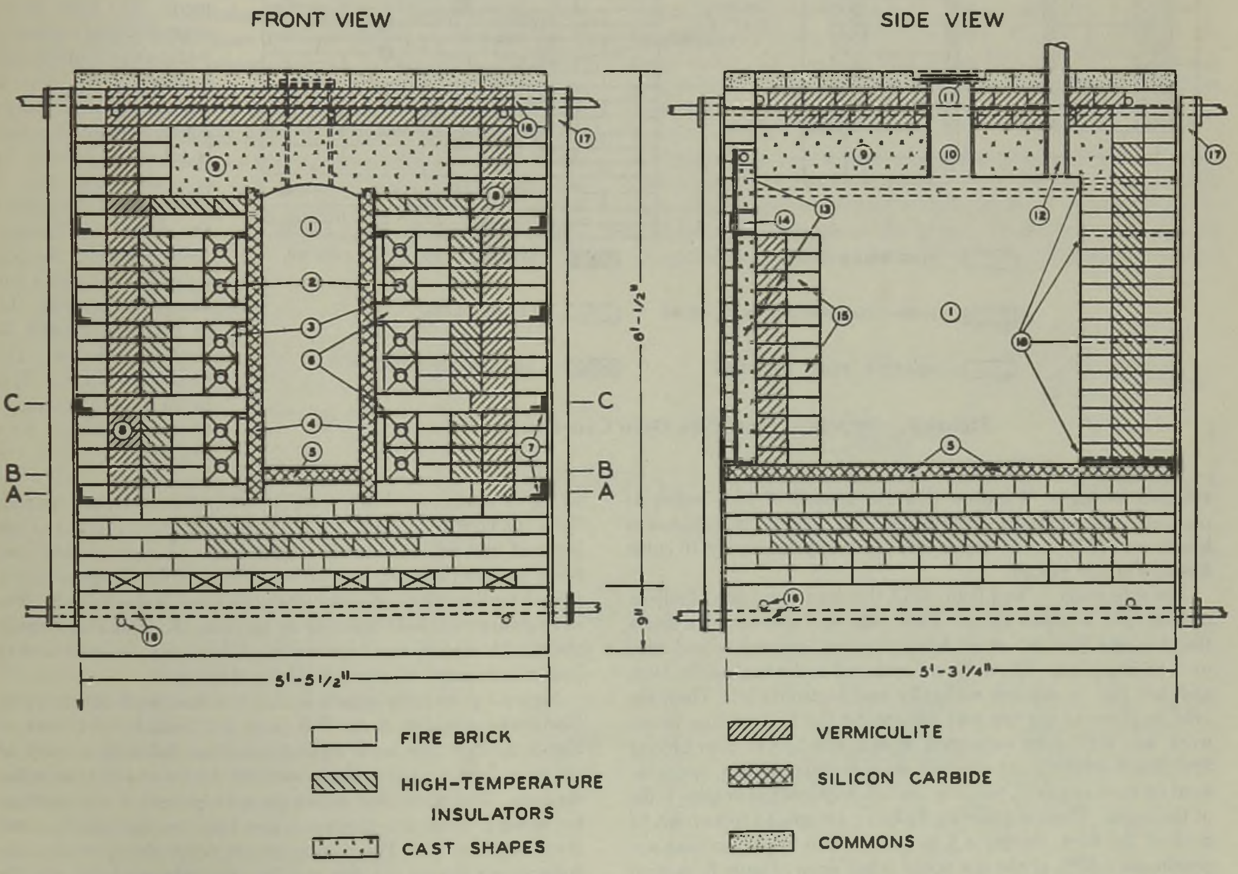

Figure 2. Sketch of Slot-Type Experimental Coke Oven

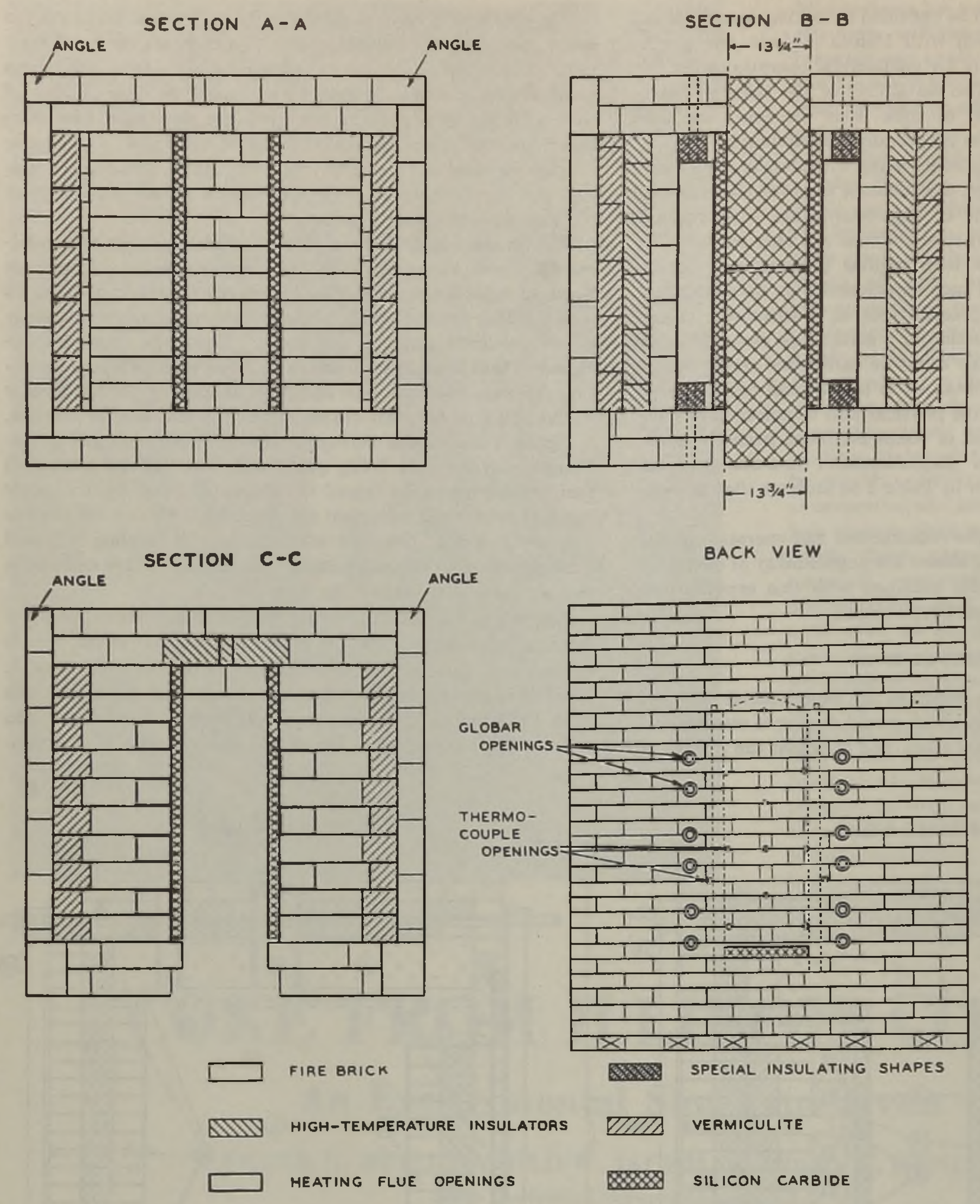

**Figure 3. Details of Slot-Type Oven Construction**

structed averages 14 inches in width instead of 13.5 inches as planned. The charging space in the oven chamber is 36 inches in length and 35 inches in depth, and holds approximately 10 cubic feet of coal per charge.

The side walls, 4, and floor, 5, of the oven are made of silicon carbide tile, 2 inches thick. Each side wall consists of a single tile, and the floor is formed from two tiles laid end to end with overlapping joint. The walls are anchored at the back of the oven and left free to expand vertically and horizontally. They are held in place at the top and bottom by the surrounding brickwork, and are further supported on each side by two rows of long firebrick, 6, which touch the oven walls and are, in turn, strengthened by steel angles, 7, running the full length of the outside walls of the oven. These supporting firebrick are spaced from front to back of the flues, leaving 4.5 inches between bricks, so that approximately 50% of the flue space is left open (Figure 3, section *C-C*). These flue openings are staggered in the two rows of supporting brick in each flue. This leaves the three sections of each flue closely interconnected and allows the heat to equalize from top to bottom of each oven wall. The oven chamber is surrounded on the sides and top by vermiculite insulation, 8. This insulation acts not only as a heat baffle but, being soft, as a cushion against thermal expansion or swelling pressures which otherwise might crack the silicon carbide walls.

The top of the oven chamber, 9, is cast of refractory concrete. Coal is charged through a 6-inch pipe, 10, extending through the casting, and a 6-inch blank flange, 11, serves as a charge hole cover. Gas escapes from the oven through a 3-inch pipe, 12, extending through the top and connected to the by-product recovery equipment. The back of the oven chamber consists of permanent brickwork, whereas the front is covered by a refractory concrete door, 13, which is raised or lowered by a chain hoist and is mudded into place before the oven is charged. After charging, the coal is leveled through a rectangular opening, 14, in the door located 35 inches above the chamber floor. This level bar opening is then bricked and mudded. Between the door and the coal charge a temporary brick wall, 15 (9 inches in depth), extends from the floor to the coal level. This wall, which consists of one layer of firebrick next to the charge and one layer of insulating brick next to the door, is removed before a coke charge is pulled, and is replaced immediately after the oven is discharged. The oven structure is held together by tie rods, 16, extending through the top brickwork and foundation. These rods are anchored to heavy buckstays, 17, at each corner of the oven.

Figure 3 gives more details of the oven brickwork construction. Horizontal sections *A-A*, *B-B*, and *C-C*, which refer back to Figure 2, show the brick arrangement just below floor level, at the oven floor, and at a plane between the lower and middle flue sections. The back view shows the arrangement of the openings for heating units and thermocouples into the heating flues and the oven chamber. Thermocouples are never placed in all of the holes shown during any one run, but the holes are built into the oven to be available when and if desired.

Table I. Comparison of Results in a Pilot Plant Coke Oven with Those in Commercial Ovens

| | Series 1 | | | Series 2 | | | Series 3 | | | Series 4 | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Run No. | S1 | S2 | C1[a] | S12 | C2[b] | C3[c] | S23 | S24 | C4[d] | S34 | S35 | C5[e] |
| Blend No. | 1 | 1 | 2 | 3 | 3 | 3 | 4 | 5 | 4 & 5 | 6 | 6 | 6 |
| Bulk density, lb.[f] | 49.0 | 49.2 | 49.0 | 47.5 | ... | ... | 48.5 | 52.3 | 48.0 | 52.7 | 52.0 | 49.0 |
| Sizing[g] | | | | | | | | | | | | |
| −8 mesh | 84.9 | 84.9 | ... | 83.9 | ... | ... | 77.6 | 82.3 | 75.0 | 68.4 | 61.6 | 75.0 |
| −20 mesh | 52.9 | 52.9 | ... | 47.8 | ... | ... | 43.6 | 51.6 | ... | 39.6 | 35.6 | ... |
| Flue temp., ° F. | | | | | | | | | | | | |
| Initial | 1600 | 1600 | ... | 1600 | ... | ... | 1600 | 1600 | ... | 1600 | 1600 | ... |
| Final | 2000 | 1850 | ... | 1850 | ... | ... | 1850 | 1850 | 2325 | 1850 | 1850 | 2340 |
| Final coke temp., ° F. | 1954 | 1824 | 1800[h] | 1802 | 1845 | 1840 | 1799 | 1787 | 1790 | 1789 | 1772 | ... |
| Penetration[i] | 1.56 | 1.17 | 1.07 | 1.18 | 1.07 | 1.07 | 1.19 | 1.06 | 1.085 | 1.07 | 1.04 | 1.085 |
| Tar yield[j] | 5.3 | 8.4 | 8.1 | 6.0 | ... | ... | 6.3 | 7.2 | 8.2 | 7.6 | 7.6 | 7.44 |
| Gas yield[k] | 3115 | 2965 | 2929 | 2721 | ... | ... | 3057 | 3156 | 2915 | 2827 | 2892 | 2835 |
| Coke yield[l] | | | | | | | | | | | | |
| Total | 73.2 | 72.5 | 72.6 | 71.2 | 71.5[m] | 71.5[m] | 71.3 | 73.5 | 71.8 | 71.7 | 71.7 | 71.3 |
| Furnace coke (+ 1 in.) | 69.8 | 70.0 | 67.3 | 67.0 | 66.1 | 66.1 | 68.2 | 70.3 | 66.2[n] | 67.2 | 67.2 | 64.1[n] |
| Breeze | | | | | | | | | | | | |
| −3/8 inch | ... | ... | 2.21 | ... | 2.6 | 2.6 | ... | ... | ... | ... | ... | ... |
| −1/2 inch | 1.8 | 1.6 | ... | 3.3 | ... | ... | 2.0 | 2.2 | ... | 3.0 | 3.0 | ... |
| −5/8 inch | ... | ... | ... | ... | ... | ... | ... | ... | 3.1 | ... | ... | 4.2 |
| Apparent sp. gr. | 0.893 | 0.895 | 0.946 | 0.83 | 0.86 | 0.84 | 0.83 | 0.86 | 0.85 | 0.87 | 0.86 | 0.88 |
| True sp. gr. | 1.92 | 1.92 | ... | 1.94 | 1.93 | 1.90 | 1.90 | 1.90 | 1.89 | 1.93 | 1.96 | 1.89 |
| Porosity, % | 53.5 | 53.4 | ... | 57.0 | 55.4 | 55.8 | 56.4 | 54.6 | 55.0 | 55.0 | 56.1 | 53.4 |
| Volatile matter, % | 1.5 | 1.1 | 1.3 | 1.2 | ... | ... | 1.1 | 1.2 | 0.8 | 1.0 | 0.9 | 0.8 |
| Shatter test | | | | | | | | | | | | |
| % over 2 in. | 47.6 | 60.4 | ... | 69.6 | 76.2 | 75.6 | 54.4 | 60.9 | 59.6[o] | 74.6 | 79.4 | 79.1[o] |
| % over 1 1/2 in. | 73.4 | 83.3 | ... | 86.3 | 88.1 | 90.0 | 80.3 | 82.0 | ... | 86.7 | 87.7 | ... |
| Tumbler test | | | | | | | | | | | | |
| % over 1 in. | 32.0 | 47.7 | 49.8 | 46.7 | 49.5 | 51.3 | 40.7 | 45.6 | 47.9 | 37.7 | 36.2 | 37–41 |
| % over 1/4 in. | 66.0 | 69.1 | 67.7 | 65.5 | 67.2 | 66.5 | 65.1 | 66.9 | 66.8 | 56.8 | 58.6 | 58–63 |

[a] Average of 3-month commercial operation.
[b] Average of two commercial ovens.
[c] Average of three commercial ovens.
[d] Average of 4-month commercial operation.
[e] Average of 1-month commercial operation.
[f] Pounds of coal per cu. ft. as charged to oven.
[g] Screen analysis of coal as charged to oven.
[h] Estimated.
[i] Width of oven in inches divided by coking time in hours.
[j] Gallons of dry tar per ton of coal as charged.
[k] B.t.u. per pound of coal as charged (includes light oils).
[l] Dry coke, % of coal as charged.
[m] Calculated.
[n] Refers to yield of furnace coke, +1 1/4 inch instead of +1 inch.
[o] Corrected.

## TEMPERATURE CONTROL

Accurate control of the temperature and heating rate of the coal in the oven is maintained by the use of Globar heating units powered from a three-phase 230-volt 60-cycle source through a 50 kv.-amp. tap transformer as shown in the wiring diagram of Figure 4. Six AT type Globar brand nonmetallic heating elements (2, Figure 2), 67 inches long and having a middle heating section 36 inches in length and 1.25 inches in diameter, designed to carry a capacity load of 100 amperes at 136 volts, are placed horizontally in each flue and spaced as shown so that heat may be applied uniformly from top to bottom of the oven walls. In each of the top flue sections the two Globar elements are connected in series, and the two units thus formed are connected in parallel across one secondary of the three-phase tap transformer. In the center and bottom flue sections the Globars are connected in the same manner across the other two secondaries. With this hookup are formed, essentially, three independently controlled single-phase circuits of approximately 16.7 kv.-amp. each, which have proved adequate to provide uniform temperature in the oven chamber. Each Globar element is supported at the front and rear of the oven in special insulating shapes (3, Figure 2) as provided by the vendor of the Globar heating elements.

Flue temperatures are controlled by a Wheelco Capacitrol which is actuated by a No. 8 gage, chromel-alumel thermocouple placed in the center flue section on one side, and adjacent to but not touching the oven wall. This thermocouple activates the three-phase primary circuit. No appreciable temperature difference has been found to exist between the two flues, and thus it was not necessary to provide a means of controlling each of the flues independently. Temperatures inside the oven are recorded by a four-point Brown recording pyrometer attached to No. 14 gage chromel-alumel thermocouples inserted through the back of the oven chamber (18, Figure 2). Three thermocouples are located just inside the silicon carbide side wall near the top, center, and bottom of the coal charge, and extend lengthwise approximately to the center of the oven. Another is placed in the exact center of the coal charge, and a fifth is located in the free gas space above the coal. Temperatures recorded at these points show the progress of temperature change throughout the carbonizing period.

Figure 5 is a photograph of a typical time-temperature chart. This chart records a run in degrees centigrade, and the temperatures should not be confused with those on the Fahrenheit scale used otherwise throughout this paper. Total elapsed time for the carbonization period is 13 hours 10 minutes. Curve (1) indicates

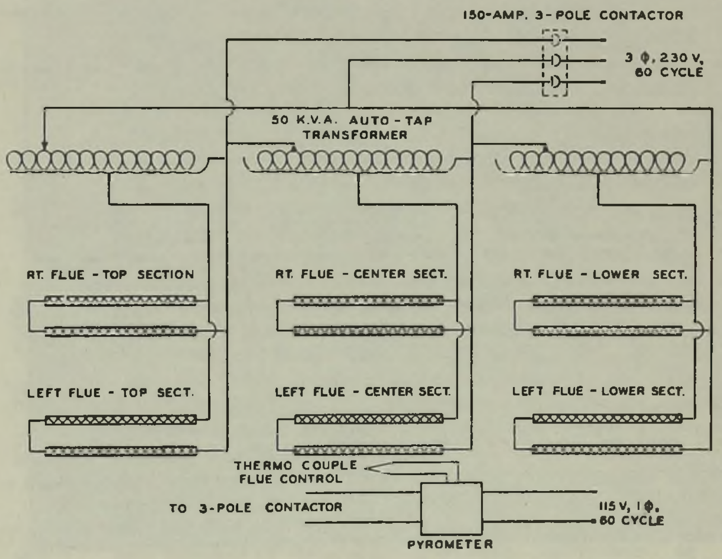

Figure 4. Wiring Diagram for Slot-Type Experimental Coke Oven

the temperature of the gas in the free space above the coal charge. The thermocouple in use at the beginning of the operation was evidently defective and was reading too low. It was replaced after 1.75 hours by a new thermocouple. Curves (2), (3), and (4) represent, respectively, the temperatures of thermocouples placed at the top, middle, and bottom of the charge next to the side wall. These curves are representative of normal charts. At the early part of the run the highest temperature along the oven wall is recorded at the top of the charge and the lowest temperature at the bottom. All temperatures rise in practically parallel straight lines for about 11 hours, after which the temperature at the center crosses over and becomes the highest. Curve (5) indicates the temperature at the approximate geometric center of the charge. Here the temperature remains constant at about 125° C. (257° F.) for the first 5 hours, rises 100° C. (180° F.) in the next 2 hours, then 700° C. (1260° F.) in the next 5 hours, and finally reaches the temperature of the charge at the side wall. Curves (4) and (5) are recorded by the No. 4 position on the temperature recorder by connecting it alternately with thermocouples 4 and 5. The circled points on the chart indicate the continuation of the curve for thermocouple 4, as shown by occasional recordings, while thermocouple 5 is being recorded continuously.

### OPERATION OF OVEN

In operating the small scale slot-type oven, various charging temperatures and final flue temperatures have been tried. In all comparative tests an attempt is made to duplicate the average heat penetration through the charge and the average final coke temperature as attained by commercial batteries. As the silicon carbide walls of the experimental oven have a higher thermal conductivity than the silica brick walls of large scale ovens, it is possible to obtain approximately the same average penetration rate at a much lower flue temperature in the experimental oven than is required in commercial ovens. Results that duplicate closely those of commercial practice have been obtained by charging the oven at an initial flue temperature of 1600° F. and raising this temperature 30° F. per hour to a maximum of 1850°. The coking time under these conditions is found to be 12.75 to 13.5 hours, or the average penetration is 1.04 to 1.10 inches per hour, depending upon such factors as bulk density, moisture content, and plastic characteristics of the coal. The final average coke temperature is 1770–1800° F.

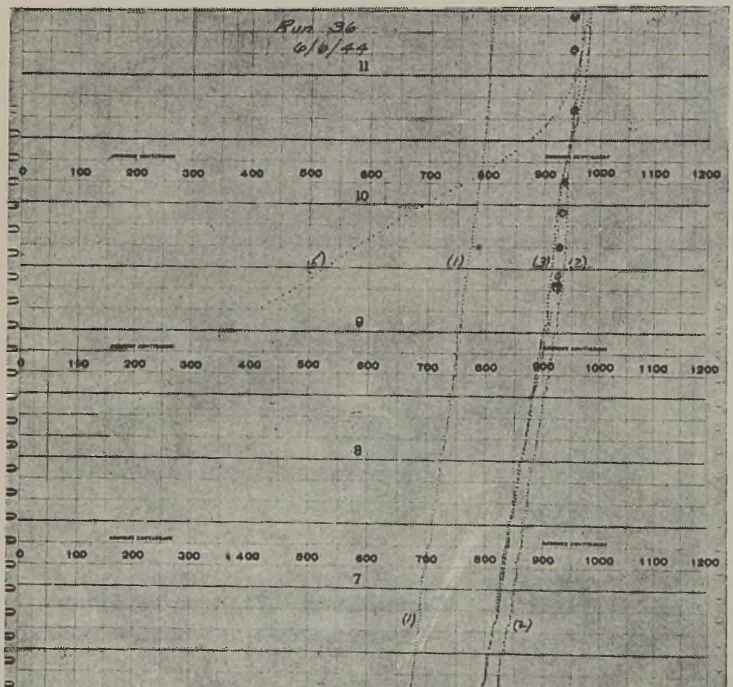

Figure 5. Time-Temperature Recording Chart

The same by-product recovery equipment is used on the slot oven that was employed with the experimental sole-flue oven (*3*). When a test run is started, the tap transformer is set at approximately 70% of rated capacity on all heating sections, and the gas exhauster is started with the by-pass open. A charge of 10.1 cubic feet (approximately 500 pounds) of coal is dumped from an overhead hopper through the charge hole and leveled in the oven. Gases are vented to the outside until the level and charge holes are sealed. The gas is then pumped through the purifying equipment by the exhauster. The initial quenching effect of the coal on the flue temperature is insignificant, and it is believed that the unit has sufficient capacity to maintain a much higher initial charging temperature, although no initial temperature above 1700° F. has been tried. As in operating the sole-flue oven (*3*), a constant pressure of 0.02 inch of water is maintained in the oven chamber and approximately 0.5 inch of water at the meter outlet.

The setting of the tap transformer for each of the three heating sections is changed from time to time as required to maintain a uniform wall temperature from the bottom to the top of the oven charge.

Rate of gas evolution is essentially constant until the plastic zone reaches the center of the charge. This rate increases gradually while the center is heating, then gradually decreases. The B.t.u. value of the gas decreases slowly from approximately 850 until the plastic zones meet, increases slightly over a short period, then drops sharply to about 300.

In all tests coking is continued until gas evolution has dropped to the rate of 50 cubic feet per hour. The oven is then opened, the brick retaining wall is removed, and the coke is pulled and quenched. The pyrometer temperature controller is set back to 1600° F., where it is maintained during all idle periods, the power is cut to 25% of rated capacity, and the fire brick retaining wall is replaced inside the oven door. Tar yield, gas make, and coke yield are computed as in the sole-flue oven tests (*3*).

Shatter and tumbler tests of the coke produced are made in accordance with standard methods adopted by the American Society for Testing Materials (*1*, *2*).

### COKING RESULTS ON DUPLICATE SAMPLES

The ability of the experimental oven to reproduce coking results under closely controlled operating conditions is shown in Table II; results are given of duplicate runs on each of two coal blends. Blend A is a mixture of Illinois and eastern coals, and blend B is all eastern coal. Operating conditions, such as coking time, rate of heat penetration, and final coke temperatures, were kept constant throughout these four runs. The degree of pulverization and the bulk density of the coal were as uniform as could be maintained experimentally.

Table II shows that coke yields checked within 0.5%. Of the physical tests, the closest checks were obtained on tumbler "stability", which is widely used in the metallurgical coke industry as an index of coke quality. Other physical properties such as apparent gravity, shatter test, and coke sizing also checked closely.

The yields and quality of the gas evolved during the coking period are shown. In Figure 6 the cubic feet of gas evolved during each hour of the coking period and the B.t.u. value of the gas are plotted from experimental data taken during both sets of duplicate runs. B.t.u. values are not shown for the gas beyond the tenth hour. Gas evolved during the balance of the coking period is very high in hydrogen, and the calorimeter is not adjusted to read accurately in this low range. These curves are typical of the results obtained under normal operating conditions.

Because of the close control of operation possible with the experimental oven, which cannot be realized in a gas-heated commercial size oven, the results on the experimental oven have been shown to be more dependable and more easily duplicated than those obtained from individual ovens of a commercial battery.

### EXPERIMENTAL AND COMMERCIAL RESULTS

The extent to which the design of the oven is successful in permitting the duplication of commercial results is shown in Table I, which gives the results of four representative series of tests comparing experimental and commercial operations.

In evaluating coke quality the producers consider the shatter and tumbler tests to be most important. Special emphasis is given to the tumbler "stability" or the percentage of coke remaining over one inch in size in the tumbler test. Shatter tests are sometimes misleading, as in the case where larger pieces of soft coke give a higher shatter test than smaller pieces of a harder coke and thus indicate a superiority not borne out by use in the blast furnace. From the standpoint of production the yields of furnace coke and breeze require careful attention.

Table II. Duplicate Runs on Pilot Oven

| | Blend A | | Blend B | |
|---|---|---|---|---|
| | No. 113 | No. 116 | No. 118 | No. 119 |
| Coke analysis, % | | | | |
| Volatile matter | 1.2 | 1.1 | 1.7 | 1.6 |
| Fixed carbon | 90.9 | 91.3 | 92.1 | 92.1 |
| Ash | 7.9 | 7.6 | 6.2 | 6.3 |
| Sulfur | 0.83 | 0.73 | 0.68 | 0.76 |
| Coke yields, % of dry coal | | | | |
| Total | 71.7 | 72.2 | 73.3 | 72.8 |
| Furnace (+1 in.) | 68.7 | 68.7 | 69.9 | 69.4 |
| Nut (1 × 1/2 in.) | 0.9 | 1.0 | 1.0 | 1.2 |
| Breeze (−1/2 in.) | 2.1 | 2.5 | 2.4 | 2.2 |
| Coke screen test, % of coke | | | | |
| Total +4 in. | 4.1 | 1.8 | 2.8 | 2.8 |
| Total +3 in. | 31.6 | 29.2 | 29.7 | 25.2 |
| Total +2 in. | 79.3 | 78.2 | 77.1 | 75.4 |
| Total +1 in. | 95.8 | 95.2 | 95.4 | 95.3 |
| Av. size, in. | 2.61 | 2.54 | 2.55 | 2.48 |
| Tumbler test | | | | |
| Stability (+1 in.) | 55.9 | 55.4 | 55.0 | 55.3 |
| Hardness (+1 1/4 in.) | 69.2 | 68.9 | 67.9 | 69.6 |
| Shatter test | | | | |
| % of +2 in. | 64.0 | 68.2 | 65.3 | 64.8 |
| % of +1 1/2 in. | 88.8 | 87.8 | 88.9 | 87.0 |
| Apparent gravity | 0.824 | 0.825 | 0.842 | 0.838 |
| Gas | | | | |
| Cu. ft./lb. dry coal | 6.50 | 6.42 | 6.14 | 6.15 |
| B.t.u. | 486 | 496 | 545 | 541 |
| B.t.u. in gas/lb. coal | 3159 | 3184 | 3346 | 3327 |

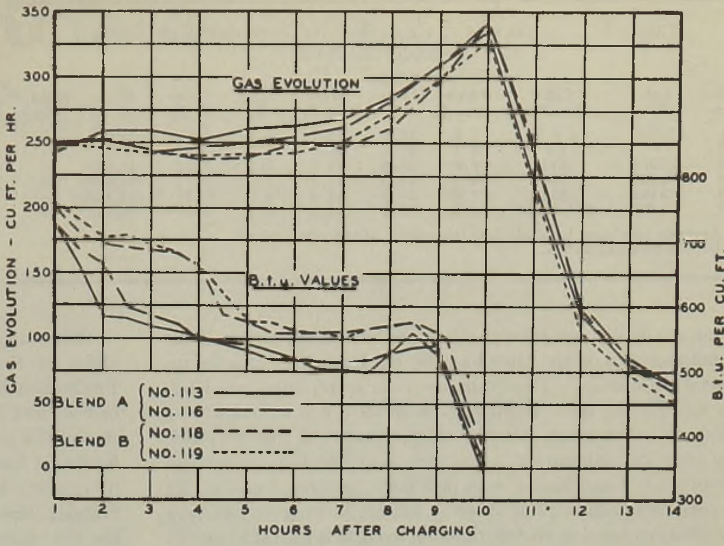

**Figure 6. Gas Evolution and B.t.u. Value**

In studying the comparison of results in Table I, it is noted that experimental oven runs are compared with average commercial results over a period of one or more months. This is due to the inconsistency of coking results from individual commercial ovens.

It is probable that a commercial oven coal charge of 17 or more tons is not entirely uniform throughout, in either physical or chemical properties. The bulk density of the coal is largely controlled by moisture and size composition, both of which may vary within wide limits in different ovens. The bulk density varies from one part of the oven to another as a result of the method of coal charging and is probably greatest at the bottom of the oven under the charge holes. The coal blend also varies slightly in different ovens or parts of ovens due to mechanical difficulties in blending coals and to size segregation. Thus it is difficult, if not impossible, to obtain a 500-pound sample of coal for the experimental oven which is an exact duplicate of the coal in any one commercial oven.

Also, the temperature control of any two ovens in a commercial battery is such that the rate of heat input in one oven varies more or less from that of another oven. Even though the length of the heating cycle is the same for each oven, two adjacent ovens in the same battery are not charged at the same time, and the oven walls cannot be kept at identical temperatures throughout the greater part of the coking period.

On account of the variation in coal charges and heating conditions mentioned above, it seems evident that the degree of accuracy which may be obtained in comparing experimental oven results with average commercial results is a function of the accuracy of experimental sampling and of the duplication of average operating conditions. Therefore, it is believed that where proper care is taken in sampling a coal blend and in evaluating average operating conditions, the results obtained by coking this sample in the experimental oven operating under exact temperature control will compare closely with the average results obtained in a commercial oven battery over an extended period of time. Results obtained from any single commercial oven or any group of ovens taken over a single day's operation will not necessarily duplicate the experimental oven results.

In the four series of comparisons shown in Table I, data for the runs in the experimental oven (prefix S) were obtained in our laboratories while data for the runs in commercial ovens (prefix C) were furnished by the cooperating industrial organizations. As would be expected, certain items of data taken in our laboratories

TABLE III. ANALYSIS OF COAL BLENDS DESIGNATED IN TABLE I (AS-RECEIVED BASIS)

| Blend No. | Lab. No. | Coke Run No. | Moisture, % | Volatile Matter, % | Fixed C, % | Ash, % | Total S, % | B.t.u. per Lb. | B.S.I.[b] No. |
|---|---|---|---|---|---|---|---|---|---|
| 1 | C3002 | S1 & S2 | 2.6 | 30.3 | 60.7 | 6.4 | 0.97 | 14,063 | 6 |
| 2 | [a] | C1 | 3.1 | 29.6 | 61.6 | 5.7 | 0.79 | .... | . |
| 3 | C3078 | S12 | 7.0 | 25.5 | 60.0 | 7.5 | 0.74 | 12,899 | 3 |
| 4 | C3187 | S23 | 3.8 | 28.5 | 62.0 | 5.7 | 0.71 | 13,927 | 6 |
| 5 | C3191 | S24 | 2.5 | 28.4 | 63.9 | 5.2 | 0.64 | 14,148 | 6 |
| 6 | C3263 | S34 & S35 | 3.5 | 28.1 | 60.3 | 8.1 | 0.76 | 13,388 | 4 |

[a] Analysis furnished by analytical laboratory of industrial plant.
[b] British Swelling Index.

are not available from commercial operation. Also, certain items are not recorded on the same basis by our laboratory and the industrial companies. Thus, furnace coke is reported as $+1^{1}/_{4}$ inch size for the commercial runs in series 3 and 4, but as +1 inch in all other cases. Also, breeze is reported as the $-^{1}/_{2}$ inch coke from our laboratory, $-^{3}/_{8}$ inch coke for the commercial runs in series 1 and 2, and $-^{5}/_{8}$ inch coke for series 3 and 4. As the coke from commercial ovens is subject to rougher handling than that produced in an experimental oven, it is logical to expect that the percentage of breeze will be slightly higher than that obtained from a duplicate run in the experimental oven.

The principal difference in operation between runs S1 and S2 is in the coking time and appears in the "penetration" values. S1 was coked in 9 hours. This was considered too rapid a rate, the heating schedule was changed, and S2 was coked in 12 hours. This slower rate gave a penetration within 10% of the commercial rate. The effect of too rapid a coking rate on sample S1 is shown in the resulting lower values for shatter and tumbler tests for this run in comparison with the values for the same tests for runs S2 and C1.

The coal used in sample S12, series 2, had an unusually high moisture content, as shown in Table III. This high moisture value is reflected in the low bulk density of the charge, and may be responsible for the slightly low shatter and tumbler test values and also for the relatively high percentage of breeze.

Coal for runs S23 and S24, series 3, was taken as a single sample representative of commercial operation yielding the average results shown under C4. One portion of this sample was used without air-drying in run S23. Another portion was partially air-dried and used in run S24. Analyses of the coal used in these two runs (Table III) indicate that they were not entirely uniform. Also, the heating rate was reduced during run S24 to give a penetration more nearly comparable with plant practice during the period when data listed under C4 were collected. The results of this change in operation are evident in the closer agreement between data of S24 with C4 than was obtained between S23 and C4.

Even though there is some difference in size composition of the coals used in runs S34 and S35 and that shown as an average commercial value under C5, the results given under series 4 compare quite closely throughout.

Table I includes also data on the tar and gas yields obtained as by-products of the coking operation. Particularly during the early operation of the experimental oven, difficulty was encountered in obtaining checks on tar yields. This appears to be due to the inability to keep the tar held in the recovery system at a constant value. No appreciable trouble was encountered in getting checks on the over-all thermal values of the gas yields from comparable runs through the experimental oven.

Experience to date with this experimental oven has demonstrated that when blends of coals are coked in it under conditions rigidly controlled to duplicate bulk densities, average penetrations, and final temperatures of commercial ovens coking the same blends, the physical and chemical properties of the coke produced in the experimental oven will check closely the averages of the respective properties of the coke produced in commercial ovens. This is true not only with Illinois coal blends, but with eastern coal blends as well. Series 2, Table I, shows coking results from an Illinois coal blend, and series 1, 3, and 4 are the results of blends of all eastern coals. Thus, this experimental slot-type oven may be used to predict accurately the physical and chemical properties of the coke which will result from the carbonization of any given blend of coals in a commercial installation.

## ACKNOWLEDGMENT

This study was made possible through the assistance of the Office of Production Research and Development of the War Production Board, Washington, D. C. Valuable counsel was received from A. C. Fieldner, U. S. Bureau of Mines, in the initiation of the project. M. D. Curran, Coal Carbonizing Company, furnished fabricated steel for oven construction and for coke and by-product testing. Walsh Refractories Corporation furnished firebrick, bonding mortar, and refractory insulating brick. Without the extensive cooperation of Koppers United Company and the Inland Steel Company, it would have been impossible to compare the results of experimental work with that of commercial operation. The Chicago, Wilmington, and Franklin Coal Company, the Bell and Zoller Coal Company, the Franklin County Coal Corporation, and the Sahara Coal Company were generous and cooperative in furnishing samples of coal. Coal and coke analyses were made under the direction of O. W. Rees, and tar and by-product analyses under the direction of G. R. Yohe, both of the Illinois State Geological Survey. To all of these organizations and individuals we express our sincere appreciation.

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# Predicting Volume Increase of Perbunan Compounds in Petroleum Products—Correction

My attention has been called to an error which appeared on Figure 1 of my article (page 224) in the March, 1945, issue of INDUSTRIAL AND ENGINEERING CHEMISTRY. Starting from the extreme left of the figure, the units on the abscissa should be 30, 40, 50, 60, 70, 80, 90, 100% Perbunan by Volume (*P*).

R. M. HOWLETT

ESSO LABORATORIES
STANDARD OIL DEVELOPMENT COMPANY
LINDEN, N. J.

.....

# Fluidized Fixed Bed—Correction

On page 332 of this article [IND. ENG. CHEM., 37, No. 4 (1945)] the photograph has been given the wrong caption. The plant pictured is the world's smallest fluid cracking unit now commercially producing aviation gasoline. It is being operated by the Frontier Refining Company.

CHARLES L. THOMAS

UNIVERSAL OIL PRODUCTS COMPANY
CHICAGO, ILL.

# Moisture Relations of Mixed Fertilizers

## INFLUENCE OF NITROGENOUS MATERIALS

JOHN O. HARDESTY, J. Y. YEE, AND KATHARINE S. LOVE

*Division of Soil and Fertilizer Investigations, U. S. Department of Agriculture, Beltsville, Md.*

**The average hygroscopicity of 1943–44 fertilizer mixtures was not appreciably different from that of mixtures made during the preceding season, even though ammonium nitrate had largely replaced sodium nitrate as a nitrogen carrier. Exceptions occurred in mixtures containing large amounts of materials such as manure salts, urea, or sodium nitrate in combination with ammonium nitrate. The moisture content of most fertilizer mixtures is sufficient to dissolve all of the ammonium nitrate commonly present. The high solubility of ammonium nitrate in conjunction with its reaction in solution with other common salts, such as potassium chloride and potassium sulfate, greatly diminishes the unfavorable influence which it would otherwise have on the hygroscopicity of most mixtures. Mixed fertilizers that are unsatisfactory from the standpoint of moisture content may be divided into three classes: (1) those that are undesirably wet due to an increase in volume of the liquid phase as a result of the highly soluble salts going into solution; (2) those with insufficient initial moisture to allow solution of hygroscopic soluble salts, thereby preventing complete curing of the mixture; and (3) those that are hygroscopic through a combination of incompatible materials or the presence of large quantities of hygroscopic salts in the solid state. An optimum moisture content at mixing time is, therefore, highly important to the general physical condition of fertilizer mixtures containing the usual quantities of very soluble salts. Observations at the factory on the physical condition of mixtures with respect to moisture absorption are correlated with laboratory values on the equilibrium moisture content of the same mixtures in order to facilitate adaptation of the laboratory procedure in forecasting the hygroscopic behavior of mixtures before they are produced in large tonnage.**

EARLY in 1943, when it became apparent that a considerable tonnage of ammonium nitrate would become available to the fertilizer industry, this laboratory initiated an investigation on the use of ammonium nitrate in complete fertilizer mixtures. The first report on these studies (*1*) presented data on the hygroscopic properties of fertilizer mixtures prepared in the laboratory according to the basic formulation practices of most fertilizer manufacturers. It showed the relative influence of several important variables, such as the effect of varying quantities of different nitrogen and potash carriers, on moisture absorption by fertilizers at different relative humidities. On the basis of results obtained, suggestions were offered concerning the satisfactory formulation of fertilizers containing ammonium nitrate, but the necessity was recognized for correlating the laboratory results with those obtained in the factory and on the farm.

An additional study was accordingly undertaken of some 450 mixed fertilizer samples, supplied by manufacturers and by fertilizer control stations and experiment stations of various states. These samples were about equally divided between mixed fertilizers that were sold during 1942–43 before solid ammonium nitrate was available to any appreciable extent, and those sold during 1943–44 when ammonium nitrate was available in quantity. Sodium nitrate was utilized extensively during the former period, but little or no sodium nitrate was used in mixed fertilizers during the second period. About 160 of the samples obtained from fertilizer manufacturers were accompanied with complete information with respect to formula, place, and date of manufacture, length of curing period, place of use, and the observations of those handling the fertilizer as to its physical condition with respect to moisture absorption.

The primary objects of this investigation were to use the information thus supplied by the manufacturers in developing a rapid laboratory procedure for evaluating the hygroscopic properties of commercial mixed fertilizers, and to utilize this procedure in determining the effect of varying proportions of ammonium nitrate on the hygroscopic properties of commercial mixtures.

A study was also made of the solubility of ammonium nitrate in the liquid phase of typical fertilizer mixtures and of the effect of varying the proportion of this material in the mixture on the volume of the liquid phase.

### RATING THE RELATIVE HYGROSCOPICITY

A hygroscopic salt such as ammonium nitrate will absorb moisture in a humid atmosphere until it liquefies and the vapor pressure of the resulting solution reaches equilibrium with that of the surrounding air. The behavior of a mixed fertilizer that consists of a mixture of hygroscopic and nonhygroscopic materials is quite different. If the mixture contains only a small proportion of a hygroscopic material, or mixture of materials, it may attain equilibrium with the surrounding air when the amount of moisture absorbed is relatively small. Other mixtures may absorb much larger quantities of moisture before reaching equilibrium. Fertilizer mixtures may thus be classified when their hygroscopic properties alone are considered, according to the maximum quantity of moisture they will absorb under any given set of conditions. A convenient classification divides them into the three groups of nonhygroscopic, hygroscopic, and very hygroscopic mixtures: A nonhygroscopic mixture does not absorb moisture in excess of the average moisture content normally occurring in mixed fertilizers at the prevailing humidity and temperature in sections of the country where fertilizers are most commonly used. A hygroscopic mixture absorbs moisture, under the conditions specified, in excess of the average moisture content occurring in mixed fertilizers so that the mixture is susceptible to an undesirable damp condition when the temperature and relative humidity are above the average. A very hygroscopic mixture absorbs moisture, under the conditions specified, to such an extent that the mixture is too damp for use.

Table I. Sample Distribution on Basis of Equilibrium Moisture Content at Various Relative Humidities, 30° C.

| Equilibrium Moisture Content, % | % of Samples Tested in Equilibrium with Relative Humidity of: 59% | 65% | 72% |
|---|---|---|---|
| <5 | 65 | 10 | None |
| 5–10 | 31 | 32 | 4 |
| 10–15 | 3 | 22 | 13 |
| 15–20 | 1 | 16 | 20 |
| 20–25 | None | 10 | 16 |
| 25–30 | None | 6 | 12 |
| 30–35 | None | 2 | 12 |
| 35–40 | None | 1 | 10 |
| 40–45 | None | 1 | 5 |
| 45–50 | None | None | 1 |
| >50 | None | None | 7 |
| | 100% | 100% | 100% |

Table II. Equilibrium Moisture Content at 30° C. of Mixed Fertilizers of Varying Hygroscopicity

| Sample No. | Grade | Field Observation | % Moisture in Mixture: As received | At equilibrium, with r.h. of: 59% | 65% | 72% |
|---|---|---|---|---|---|---|
| 1 | 6-14-0 | Nonhygroscopic | 2.7 | 2.7 | 4.5 | 7.9 |
| 2 | 5-10-10 | Nonhygroscopic | 7.0 | 4.2 | 7.9 | 31.2 |
| 3 | 8-8-8 | Nonhygroscopic | 5.5 | 8.0 | 18.7 | 32.8 |
| 4 | 6-8-4 | Hygroscopic | 5.5 | 10.5 | 21.8 | 34.0 |
| 5 | 10-5-10 | Very hygroscopic | 3.4 | 14.3 | 38.2 | 50.8 |

Table III. Composition of Fertilizer Mixtures (in Pounds per Ton)

| Material | No. 1 (6-14-0) | No. 2 (5-10-10) | No. 3 (8-8-8) | No. 4 (6-8-4) | No. 5 (10-5-10) |
|---|---|---|---|---|---|
| Superphosphate | 1463 | 1029 | 890 | 857 | 500 |
| Nitrogen solution | .. | 138 | ... | ... | ... |
| Urea-ammonia liquor | .. | .. | ... | 105 | ... |
| Ammonium nitrate | 115 | 25 | 200 | 118 | 412 |
| Ammonium sulfate | 385 | 168 | 440 | 180 | 289 |
| Potassium chloride | .. | 333 | 270 | 67 | 336 |
| Manure salts | .. | .. | ... | 160 | ... |
| Organic conditioner | .. | 100 | 140 | 70 | 100 |
| Hydrated lime | 37 | .. | 30 | ... | ... |
| Dolomite | .. | 200 | 30 | 356 | ... |
| Silica filler | .. | 7 | ... | 87 | 363 |

The average summer relative humidity in the section of the United States where fertilizers are most generally used varies from about 59 to 72% with an average of about 65% when calculated on the basis of an average temperature of 30° C. Very hygroscopic mixtures are likely to absorb moisture at 30° C. and a relative humidity of 65%, but few mixed fertilizers now on the market will absorb sufficient moisture at 59% relative humidity to interfere seriously with their drillability in the field.

Mixed fertilizers will absorb or lose moisture until they reach equilibrium with the humidity of the air with which they are in contact. In the method developed by Yee and Davis (*5*) for determining the equilibrium moisture content of fertilizers, 4-gram samples of the materials tested were exposed for 48 hours to circulating air in each of three closed chambers, maintained at 30° C. and at relative humidities of 59, 65, and 72%. The moisture in the samples at the beginning of the test was determined by drying in vacuum over Anhydrone for 20 hours. The moisture content at the end of the test was determined by reweighing the sample.

The rate of gain or loss of moisture under these conditions is much greater than would actually take place under commercial conditions of packaging and storage. It is necessary, however, that a laboratory method of this kind be an accelerated test if it is to have any value in forecasting the relative hygroscopic properties of commercial mixed fertilizers. As this method offered a promising laboratory procedure for rating the hygroscopic properties of fertilizers, it was used in determining the equilibrium moisture content of the commercial mixed fertilizers supplied by the fertilizer manufacturers and fertilizer control stations.

## DISCUSSION OF RESULTS

Table I shows the proportion of the total number of samples tested which fall in different ranges of moisture content at the three relative humidities used. At 65% r.h. the samples are grouped fairly symmetrically over a wide range of moisture content, an indication that the test at this relative humidity gives a more reliable index of moisture absorption than that at either 59 or 72% r.h. The results obtained with representative samples are shown in Table II. The formulas used in the preparation of the mixtures are given in Table III. As a rule mixtures that were rated in the field as being nonhygroscopic absorbed moisture during the test to give a maximum moisture content of about 20% at 65% r.h. Mixtures that were rated as being hygroscopic absorbed water to give a minimum moisture content of 20% and a maximum of 30% at 65% r.h. The very hygroscopic mixtures under the same conditions absorbed water to give moisture contents exceeding 30%.

The data and observations in Table II indicate that the relation between the hygroscopicity of the fertilizer and its equilibrium moisture content may be represented as follows:

| Type of Mixture | % Equilibrium Moisture Content at 65% R.H., 30° C. |
|---|---|
| Nonhygroscopic | Less than 20 |
| Hygroscopic | 20–30 |
| Very hygroscopic | More than 30 |

Although the determination of the equilibrium moisture content of a fertilizer at 30° C. and 65% r.h. serves to classify it with respect to hygroscopicity, there is an advantage in also making the same determination at 59 and 72% r. h. From the data obtained (Table II) at these three humidities, curves may be drawn as shown in Figure 1. These curves indicate the maximum amount of moisture that the fertilizer will absorb under equilibrium conditions at 30° C. and at any relative humidity between 59 and 72%. They supply information relative to the hygroscopic properties of a fertilizer that is not provided by a single equilibrium moisture determination at one humidity. Thus, the more or less horizontal slope of curve 1 shows that the mixture it represents does not contain any hygroscopic salt or salt pair in the solid state. Such a mixture is not rated as hygroscopic in any section of the country. Curve 2 shows that the mixture it represents does not contain any salt or salt pair in the solid state that is hygroscopic below a relative humidity of 65% but that it contains a material or salt pair that rapidly absorbs moisture above 65%. A mixture of this kind is therefore rated as satisfactory in sections of the country having an average relative humidity below 65% but not in localities where the average relative humidity is much in excess of 65%. Curve 3 shows that the 8-8-8 mixture it represents is nonhygroscopic; curve 4 shows that the 6-8-4 mixture it represents contains a sufficient quantity of hygroscopic components to make it moderately hygroscopic. The slope and location of curves 3 and 4 indicate that they represent borderline mixtures which may or may not show hygroscopic tendencies, depending on conditions under which they are packed and stored. Curve 5 shows that the 10-5-10 mixture it represents contains a large proportion of very hygroscopic materials and that they are not all in solution at the initial moisture content. Such a mixture rapidly absorbs moisture to become undesirably wet even at relative humidities below 59%. A standard laboratory test that includes equilibrium moisture absorption determinations at all three relative humidities and at 30° C. was therefore adopted for rating the hygroscopic properties of mixed fertilizers.

## HYGROSCOPIC COMPONENTS

Table IV shows the approximate proportion of hygroscopic materials in mixed fertilizers produced in 1942–43 as compared with the estimate for 1943–44. The amount of hygroscopic salts used in mixtures during 1943–44 was about 10% less than

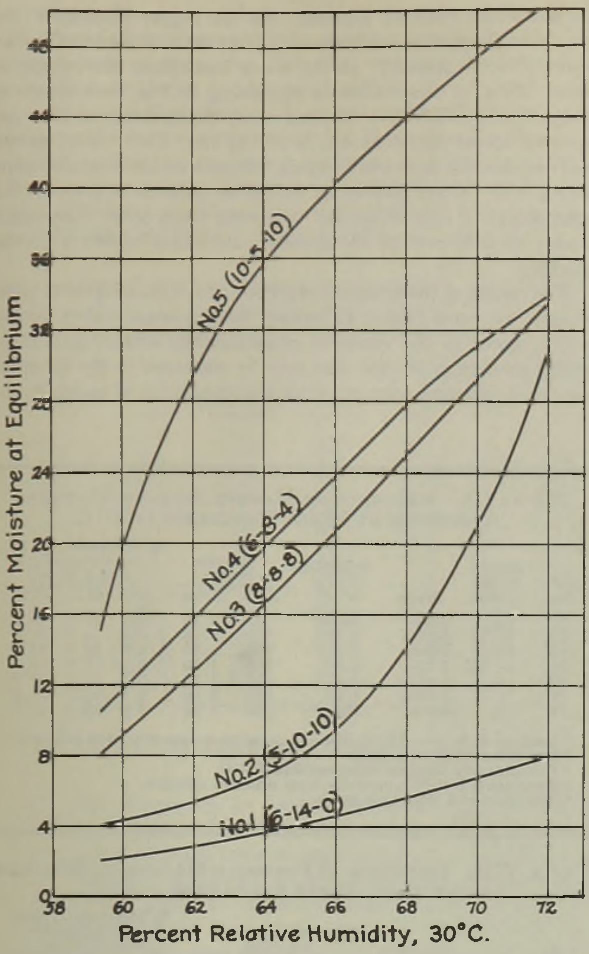


**Figure 1. Equilibrium Moisture Content of Fertilizer at Different Relative Humidities**

that used during the preceding year. Sodium nitrate has been shown to produce somewhat greater hygroscopicity than ammonium nitrate (*1*) on the basis of equal units of nitrogen in the mixture. A similar comparison on the basis of equal weights of these two nitrogen carriers in the mixture (unpublished data) also shows that sodium nitrate produces somewhat greater hygroscopicity than ammonium nitrate. Therefore, it would appear from Table IV that the hygroscopicity of 1943–44 fertilizers should not vary greatly from that of mixtures produced in 1942–43

Data on the control station samples (Table V) show that there has been no general increase in the hygroscopicity of 1943–44 fertilizers over that of the preceding year, when little solid ammonium nitrate was used. The maximum moisture value given for each relative humidity represents the highest value obtained on any sample in the set. In most cases these values are far above the average for the set, as given for each relative humidity, this indicates that they represent exceptional mixtures. Thus; the mixtures represented by the maximum values for Indiana in 1943–44, for Massachusetts and Texas in 1942–43, and for Mississippi during both seasons, are subject to poor condition through excessive moisture absorption, since they are shown to be very hygroscopic under the conditions of the laboratory test. However, the maximum values representing these exceptionally hygroscopic mixtures are in most cases lower for the past season than for the preceding season. This is a further indication that such mixtures containing ammonium nitrate will give no greater difficulty as a result of moisture absorption than those formulated with sodium nitrate before solid ammonium nitrate became available in quantity.

Table IV. Hygroscopic Materials in Mixed Fertilizers (in Short Tons)

| Material | 1942–43 | 1943–44[a] |
|---|---|---|
| Sodium nitrate | 200,000 | None |
| Ammonium nitrate | 45,000 | 200,000 |
| Urea | 30,000 | 50,000 |
| Sodium chloride[b] | 110,000 | 120,000 |
| Total | 385,000 | 370,000 |
| Mixed fertilizer | 7,577,800 | 8,000,000[c] |
| Lb. material/ton mixt. | 102 | 92 |

[a] Based on revised nitrogen supply for 1943–44, Chemicals and Fertilizer Branch, War Food Administration.
[b] From manure salts.
[c] Assuming 5% increase over 1942–43.

Table V. Comparison of Hygroscopicity at 30° C. of Mixed Fertilizers in 1943–44 and 1942–43

| Region Where Used | Year | No. of Samples | % Moisture in Mixt. at Equilibrium with: 59% r.h. Max. | 59% r.h. Av. | 65% r.h. Max. | 65% r.h. Av. | 72% r.h. Max. | 72% r.h. Av. |
|---|---|---|---|---|---|---|---|---|
| Ind. | 1942–43 | 17 | 4.7 | 2.8 | 20.7 | 6.6 | 56.2 | 23.6 |
| | 1943–44 | 15 | 18.6 | 5.5 | 30.4 | 11.8 | 47.5 | 28.5 |
| Mass. | 1942–43 | 12 | 10.7 | 5.7 | 35.1 | 17.6 | 64.0 | 29.9 |
| | 1943–44 | 12 | 8.1 | 4.7 | 24.5 | 13.6 | 38.7 | 26.3 |
| Miss. | 1942–43 | 10 | 16.8 | 8.5 | 39.2 | 26.8 | 48.5 | 34.4 |
| | 1943–44 | 18 | 10.6 | 5.5 | 32.3 | 19.4 | 41.0 | 27.7 |
| N. J. | 1942–43 | 12 | 4.7 | 2.5 | 19.4 | 9.7 | 33.8 | 21.9 |
| | 1943–44 | 12 | 7.3 | 4.0 | 16.1 | 11.0 | 31.4 | 24.4 |
| N. C. | 1942–43 | 12 | 6.0 | 4.3 | 16.2 | 8.9 | 23.7 | 16.1 |
| | 1943–44 | 12 | 5.5 | 3.7 | 13.6 | 8.6 | 22.8 | 14.9 |
| Texas | 1942–43 | 12 | 5.3 | 3.7 | 41.4 | 20.9 | 55.5 | 35.0 |
| | 1943–44 | 9 | 7.3 | 4.7 | 28.3 | 17.2 | 43.8 | 28.9 |
| Total | 1942–43 | 75 | | 4.3 | | 14.2 | | 26.4 |
| | 1943–44 | 78 | | 4.7 | | 13.9 | | 25.3 |

Table VI. Moisture Absorption by 1943–44 Fertilizers at 30° C.

| Region | No. of Samples | % Moisture in Mixt. at Equilibrium with: 59% r.h. Max. | 59% r.h. Av. | 65% r.h. Max. | 65% r.h. Av. | 72% r.h. Max. | 72% r.h. Av. |
|---|---|---|---|---|---|---|---|
| New Eng. | 26 | 8.1 | 4.0 | 26.9 | 16.7 | 59.6 | 35.0 |
| S. Atlantic | 54 | 6.4 | 4.0 | 28.3 | 10.4 | 42.2 | 18.1 |
| Mid. Atlantic | 35 | 7.3 | 3.6 | 23.4 | 10.7 | 55.5 | 24.1 |
| N. Central | 28 | 18.6 | 5.1 | 30.4 | 10.9 | 47.5 | 25.2 |
| S. Central | 13 | 6.9 | 4.5 | 29.9 | 13.4 | 37.9 | 22.1 |
| Total | 156 | | 4.2 | | 11.9 | | 23.8 |

Table VI shows the results of moisture absorption tests on 156 samples representing popular grades of fertilizer used in different sections during 1943–44. The maximum values at 65% r.h. represent mixtures that are likely to absorb moisture in warm humid weather, notwithstanding the fact that some of them were reported as satisfactory under commercial conditions of storage during the winter months when, in most areas, the aqueous vapor pressure in the atmosphere is relatively low.

### MIXTURES WITH POTASH CARRIERS

Manure Salts. Table VII gives formulation data and results of moisture absorption tests on typical samples of 1943–44 goods containing increasing quantities of manure salts and varying amounts of ammonium nitrate and $P_2O_5$. Potassium chloride supplies the remainder of the potash in all of these mixtures. Samples 16 and 29 represent mixtures that are entirely satisfactory from the standpoint of moisture absorption. While the mixtures listed in Table VII were reported as satisfactory at points of manufacture, the laboratory tests show that samples 15 and 52 are hygroscopic and that samples 27, 31, and 50 contain nearly the maximum amount of incompatible hygroscopic salts that can be tolerated.

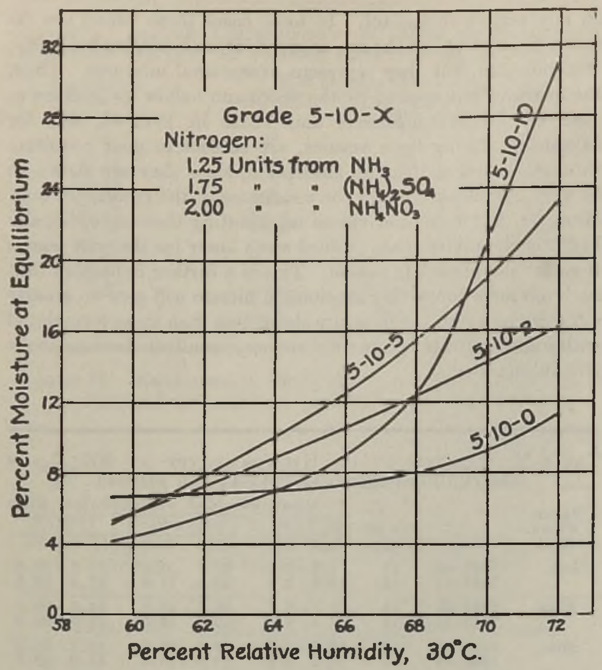


**Figure 2. Effect of Potassium Chloride Content on Moisture Absorption by Mixed Fertilizers**

**Potassium Sulfate.** The extremely low equilibrium moisture content at 65% relative humidity of the mixtures listed in Table VIII as compared with the average for 156 commercial samples (Table VI) shows the beneficial effects of potassium sulfate and of sulfate of potash-magnesia on moisture absorption by ammonium nitrate mixtures, with or without other potash carriers. This is especially true of sample 57, representing a mixture which contains approximately 4 units of $K_2O$ from 279 pounds of manure salts and 1.5 units of nitrogen from 90 pounds of ammonium nitrate.

**High-Grade Potassium Chloride.** Merz and co-workers (*3*) showed that, in the system $K^+$, $NH_4^+$, $Cl^-$, $NO_3^-$, and water, with KCl in excess at the triple salt point, the relative humidity of the air in equilibrium with saturated solution is 67.9% at 30° C. Figure 2 shows the effect of increasing amounts of potassium chloride on moisture absorption in laboratory preparations of 5-10-*x* grades of mixtures that are identical except with respect to potassium chloride content. At the higher humidities the moisture absorption increases with increase in amount of potassium chloride present; at the lower humidities the reverse is true. Thus, in these mixtures containing KCl in the solid state, the salt pair $NH_4NO_3 + KCl$ increases the tendency of the mixture to absorb moisture above 67.9% r.h. Conversely, excess potassium chloride exerts a drying influence on the mixture below 67.9% r.h. Where little or no potassium chloride is present, the ammonium nitrate or its salt pair with some other component exerts its influence on the moisture-absorbing tendency of the mixture.

The results of the moisture absorption tests on samples of commercial mixtures (Table IX) show there is considerable leeway with respect to the quantity of ammonium nitrate and high-grade potassium chloride that may be combined in the formulation of satisfactory mixtures from the standpoint of moisture ab-

TABLE VII. INFLUENCE OF MANURE SALTS ON MOISTURE ABSORPTION BY MIXED FERTILIZERS AT 30° C.

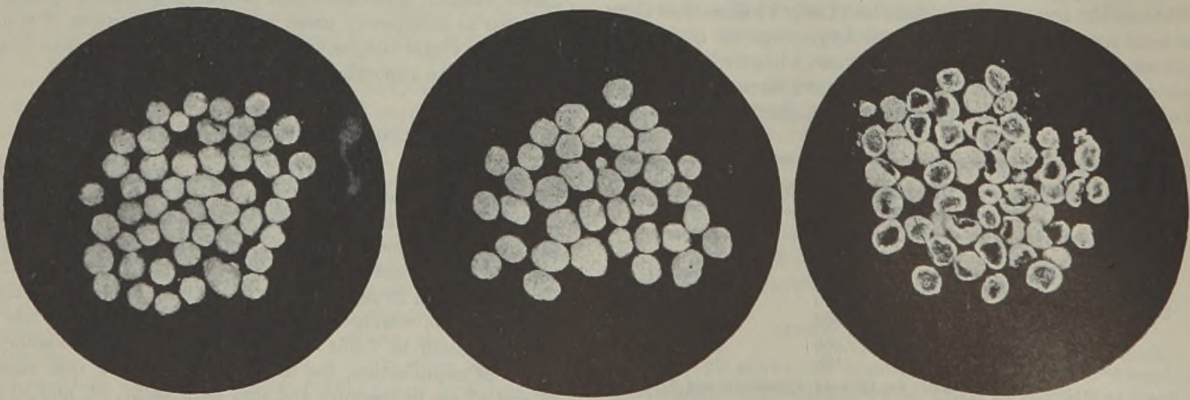
| Lab. No. | Region Where Used | Grade | $NH_4NO_3$, Units of N[a] | Manure Salts[b] |  | % Moisture in Mixt. at Equilibrium with R.H. of: |  |  |
|---|---|---|---|---|---|---|---|---|
|  |  |  |  | Lb. | Units | 59% | 65% | 72% |
| 16 | La. | 6-8-4 | None[c] | 61 | 0.75 | 3.7 | 13.4 | 22.9 |
| 29 | N. Y. | 5-10-5 | 1.1[d] | 100 | 1.25 | 3.5 | 9.5 | 22.8 |
| 52 | Ga. | 6-8-6[e] | 2.8 | 120 | 1.65 | 5.6 | 22.0 | 30.4 |
| 31 | N. Y. | 4-12-4 | 2.0 | 130 | 1.75 | 5.2 | 19.2 | 29.1 |
| 50 | Ga. | 5-10-5[e] | 2.5 | 130 | 1.75 | 6.0 | 19.7 | 26.9 |
| 27 | N. Y. | 6-12-6 | 1.3[d] | 154 | 2.00 | 4.9 | 17.3 | 31.3 |
| 15 | La. | 4-8-8 | None[c] | 233 | 3.00 | 5.9 | 28.3 | 42.2 |

[a] Balance of N from $(NH_4)_2SO_4$ and organics unless otherwise indicated.
[b] Balance of $K_2O$ from KCl.
[c] Contained 90 lb. urea-ammonia liquor.
[d] Represents $NH_4NO_3$ partially from nitrogen solution.
[e] Manufactured from base goods.

TABLE VIII. INFLUENCE OF POTASSIUM SULFATE ON MOISTURE ABSORPTION BY MIXED FERTILIZERS AT 30° C.

| Lab. No. | Grade | $NH_4NO_3$, Lb./Ton | Potash Carrier, Lb./Ton |  |  | % Moisture in Mixt. at Equilibrium with R.H. of: |  |  |
|---|---|---|---|---|---|---|---|---|
|  |  |  | KCl | $K_2SO_4$ | SPM[a] | 59% | 65% | 72% |
| 45 | 5-10-4 | 140 | 104 | 40 | ... | 4.5 | 10.3 | 17.2 |
| 57 | 4-8-6[b] | 90 | ... | ... | 182 | 3.6 | 9.3 | 15.6 |
| 59 | 3-9-9[c] | 16 | ... | 200 | 90 | 3.9 | 6.2 | 11.1 |
| 60 | 3-9-9[c] | 19 | 38 | 328 | ... | 3.7 | 5.5 | 8.7 |
| 61 | 3-9-6 | 17 | 93 | 147 | ... | 3.4 | 5.5 | 8.6 |
| 62 | 3-9-6 | 19 | 38 | 105 | 73 | 4.4 | 6.9 | 8.9 |
| 22 | 3-9-6 | 68 | 69 | 160 | ... | 3.3 | 7.8 | 12.1 |
| 38 | 3-9-6 | 90 | ... | 203 | 90 | 2.4 | 4.6 | 5.2 |
| 41 | 3-9-6 | 87 | 56 | ... | 377 | 4.2 | 8.7 | 13.1 |

[a] Sulfate of potash-magnesia.
[b] Contained 279 pounds manure salts.
[c] Contains urea-ammonia liquor.



**Before mixing** **After mixing** **Shells after curing**

**Figure 3. Behavior of Granular Ammonium Nitrate in Fertilizer Mixtures**

sorption. The high-analysis mixtures represented by samples 96, 97, and 99 were found to be hygroscopic according to the laboratory tests as shown by their high moisture content at 65% r.h. The mixtures represented by these three samples were packed in moisture-resistant bags and used in the northeastern states. Moisture analysis at bagging time, and again after farm storage periods of one month or more, gave no indication of moisture absorption. Under less favorable conditions of package protection and climate, these mixtures would be subject to poor physical condition through absorption of moisture.

Table IX. Influence of High-Grade Potassium Chloride on Moisture Absorption by Mixed Fertilizers at 30° C.

| Sample No. | Grade | $NH_4NO_3$, Lb./Ton | KCl, Lb./Ton | % Moisture in Mixt. at Equilibrium with R.H. of: 59% | 65% | 72% |
|---|---|---|---|---|---|---|
| 20 | 5-17-0 | 163 | None | 5.1 | 7.4 | 11.4 |
| 72 | 4-12-4 | 64 | 122 | 2.8 | 6.7 | 12.9 |
| 68 | 10-6-4 | 52 | 129 | 2.8 | 12.4 | 28.1 |
| 63 | 6-8-4 | 186 | 134 | 6.9 | 12.7 | 17.9 |
| 37 | 5-10-5 | 90 | 167 | 2.9 | 9.1 | 18.7 |
| 42 | 2-12-6 | 53 | 193 | 6.5 | 10.3 | 20.7 |
| 40 | 4-10-6 | 114 | 195 | 3.4 | 9.3 | 23.6 |
| 76 | 6-18-6 | 144 | 200 | 5.1 | 17.2 | 24.5 |
| 44 | 7-7-7 | 121 | 238 | 4.7 | 11.5 | 24.5 |
| 71 | 4-12-8 | 68 | 259 | 2.8 | 8.6 | 23.7 |
| 49 | 5-10-10 | 140 | 338 | 4.3 | 19.1 | 31.1 |
| 77 | 5-20-10 | 130 | 330 | 3.0 | 16.3 | 39.7 |
| 65 | 4-8-12 | 55 | 396 | 2.5 | 8.5 | 31.8 |
| 34 | 3-9-15 | 114 | 505 | 6.7 | 15.4 | 27.8 |
| 96 | 8-16-16 | 195 | 530 | 2.4 | 26.0 | 57.0 |
| 97 | 8-12-16 | 198 | 530 | 3.2 | 26.9 | 55.8 |
| 99 | 8-12-20 | 198 | 670 | 2.6 | 25.0 | 59.6 |

### SOLUBILITY OF AMMONIUM NITRATE AS RELATED TO MOISTURE ABSORPTION

Moisture absorption by mixtures increases with increase in quantity of ammonium nitrate employed; however, it is clear from the results of the tests on commercial mixtures that the increase caused by as much as 3 units of nitrogen from ammonium nitrate is not sufficient to produce unsatisfactory moisture-absorbing properties in the mixture except in isolated cases of incompatibility with other materials such as manure salts, urea, or sodium nitrate.

A previous paper (*3*) showed that most reciprocal salt pairs exhibit greater hygroscopicity than the most hygroscopic salt present in the solid phase. It is well known that most fertilizer mixtures are no less hygroscopic than the most hygroscopic salt present in the solid state. The question then arises as to why mixtures, containing ammonium nitrate added as a solid, are far less hygroscopic than ammonium nitrate itself. The answer comes from the fact that most fertilizer mixtures contain sufficient moisture to dissolve all of the highly soluble ammonium nitrate added, so that it no longer exists in the mixture as a solid phase in contact with saturated solution.

A 5-10-5 grade of fertilizer was prepared containing 3.5% moisture and 2 units of nitrogen from granular ammonium nitrate coated with 0.5% of a mixture of equal parts of petrolatum, rosin, and paraffin. One week after mixing, practically all of the solid ammonium nitrate had disappeared. The components of this mixture, with the exception of ammonium nitrate, were ground to pass a 20-mesh screen previous to mixing; the granular ammonium nitrate used was larger than 20 mesh. When the apparently whole granules remaining after a curing period of 1 week were separated, they were found to be merely hollow shells (Figure 3), consisting chiefly of the wax coating plus other ingredients of the mixture which had formed a layer on the surface of the granule during the mixing operation. Analysis showed that these shells contained less than 5% of the original nitrogen content of the ammonium nitrate. The mixture did not show an increase in moisture content during the curing period. Evidently enough initial moisture was available to dissolve all of the ammonium nitrate present. While the liquid phase of the fertilizer mixture is saturated with respect to other less soluble salts, the highly soluble ammonium nitrate is entirely in solution. Thus the hygroscopicity is dependent, in this case, on the ratio of moisture to ammonium nitrate in the mixture.

Figure 4 shows the effect of initial moisture content on the relative humidity at which a 5-10-5 grade of fertilizer begins to absorb moisture at 30° C. The mixture contained 1 unit of nitrogen as ammonium nitrate, 1.25 units as ammonia, and the remainder as ammonium sulfate. The relative humidity of the atmosphere over the fertilizer in a closed container was determined by the electric hygrometer according to the method described by Yee (*4*). The critical point representing the relative humidity at which this mixture begins to absorb moisture decreases rapidly with only slight decrease in moisture content of the fertilizer. For example, the curve of Figure 4 shows that this mixture absorbs moisture at 58% r.h. when the initial moisture content is 2%, but the same mixture does not absorb moisture at 62% r.h. when the initial moisture content is 4%. In very dry mixtures, containing only 1 or 2% of moisture at the time of mixing, there is insufficient water to dissolve all of the ammonium nitrate, the mass of the curing pile is protected against moisture absorption from the atmosphere, and the normal curing reactions do not go to completion until the fertilizer is removed for milling and bagging. This may induce secondary setting in the bag as a result of the absorption of moisture and completion of reactions that would normally occur in the curing pile.

### CHANGE IN VOLUME OF FERTILIZER LIQUID PHASE

While the use of recommended amounts of ammonium nitrate in fertilizers offers no great difficulty with respect to moisture absorption, it is frequently observed that a mixture with a relatively high moisture content may appear to become more damp with the use of increasing amounts of highly soluble salts such as urea and ammonium nitrate, even though the moisture content of the mixture does not change (*2*). This change in physical condition of the mixture is due to an increase in volume of the liquid phase of the fertilizer as a result of the highly soluble salts going into solution. It is well known that green superphosphate normally contains a larger volume of liquid phase than well-cured superphosphate. Therefore, the use of green superphosphate in conjunc-

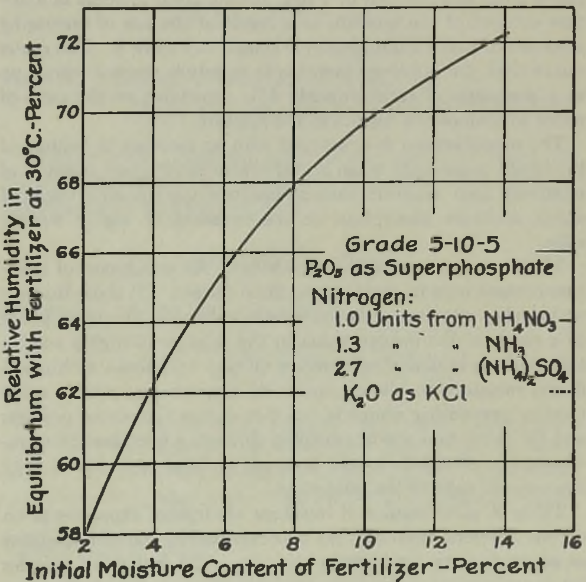


Figure 4. Effect of Initial Moisture Content on Moisture Absorption by Fertilizers

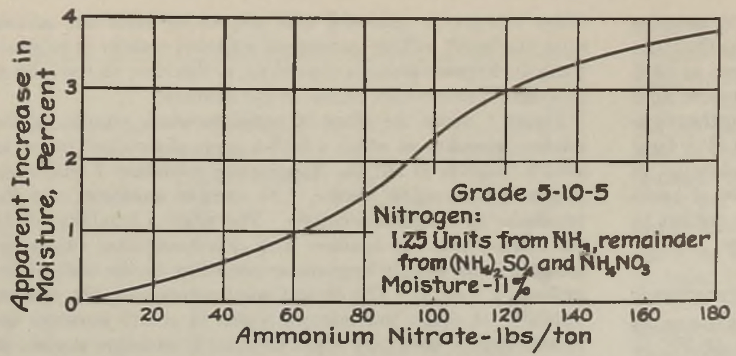


**Figure 5. Apparent Increase in Moisture Content of Fertilizers with Increasing Amounts of Ammonium Nitrate**

tion with either ammoniating solutions or solid nitrogen carriers, such as urea and ammonium nitrate, may produce an undesirably damp condition of the mixture which is not observed with the use of well-cured superphosphate. The resulting larger volume of liquid phase appears to possess about the same wetting power per unit volume as the original liquid phase of the superphosphate.

The change in volume of liquid phase in a 5-10-5 grade of fertilizer with increasing amounts of ammonium nitrate was determined by experiment. The mixtures contained 1.25 units of nitrogen from ammonia, and the balance from ammonium nitrate and ammonium sulfate. The potash was supplied by potassium chloride. Tests were made on four separate mixtures; one contained no ammonium nitrate, and the other three contained 1, 2, and 3 units of nitrogen, respectively, from ammonium nitrate. Other factors, including a moisture content of 11%, remained constant during the tests.

A portion of the liquid phase was extracted from each of the mixtures by means of hydraulic pressure. The total volume of liquid phase in each mixture was calculated from the salt and water content, the specific gravity of the extracted solution, and the moisture content of the original mixture. Increasing amounts of ammonium nitrate in the fertilizer caused an increase in volume of the liquid phase. Assuming this solution to have a wetting power equivalent to that of water, the apparent increase in moisture content of the mixture as a result of the use of increasing amounts of ammonium nitrate is shown in Figure 5. The curve shows that the apparent increase in moisture content varies up to a maximum of approximately 4%, depending on the ratio of water to ammonium nitrate in the mixture.

The manufacturer is concerned with an increase in volume of the liquid phase only when an otherwise satisfactory mixture of relatively high moisture content becomes too wet as a result of either moisture absorption or the presence of highly soluble salts.

Mixtures that are unsatisfactory from the standpoint of moisture content may be divided into three classes: (1) those that are undesirably wet due to the increase in volume of the liquid phase as a result of the incorporation in the mixture of highly soluble salts such as urea and ammonium nitrate: (2) those with insufficient moisture to allow solution of hygroscopic, soluble salts, thereby preventing complete reaction during the curing process; and (3) those that are hygroscopic through a combination of incompatible materials or the presence of large amounts of very hygroscopic salts in the solid state.

Table X gives results of moisture absorption experiments on several different mixtures that were reported by the manufacturer as unsatisfactory for bagging and use. The first three samples listed are typical of the first class of mixtures in which the combined contents of moisture and ammonium nitrate have increased the volume of liquid phase beyond the range of a satisfactory dry condition. The moisture absorption data show that these three mixtures should be satisfactory as far as hygroscopicity is concerned. The average moisture content of all the commercial samples as received was 4.6%. The average moisture content of these three unsatisfactory samples is 7.5%. This moisture was evidently in the fertilizers when they were mixed. Reduction of their moisture contents to approximately 4.6% made them appear dry and friable.

The second three samples are typical of the second class of unsatisfactory mixtures that exhibit both primary and secondary caking. After 1 to 3 months in the curing pile, these mixtures were set extremely hard and were very dry. They were susceptible to reset after bagging. The ammonium nitrate was added in the form of nitrogen solution. As the pile cooled, recrystallization of soluble salts occurred to induce caking, the normal reactions of the curing process were not completed, and additional moisture was absorbed during milling and bagging which acted to complete the reactions of curing and cause a secondary set in the bag. The addition of water during the mixing operation in sufficient quantity to allow complete curing reactions to proceed is one means of improving the condition of such mixtures.

TABLE X. MIXTURES WITH UNSATISFACTORY PHYSICAL CONDITION

| Sample No. | Grade | $NH_4NO_3$, Lb./Ton | Factory Observations | % Moisture in Mixture: As received | % Moisture in Mixture: At equilibrium, with r.h. of: 59% | 65% | 72% |
|---|---|---|---|---|---|---|---|
| 4403 | 4-12-4 | 180 | Initially wet | 6.6 | 6.3 | 16.6 | 23.8 |
| 4408 | 4-12-4 | 180 | | 8.0 | 7.9 | 17.1 | 25.5 |
| 5020 | 5-17-0 | 162 | | 8.0 | 5.1 | 7.4 | 11.4 |
| 4802 | 4-12-4[a] | 125 | Excessive set | 1.6 | 4.0 | 13.7 | 18.2 |
| 4805 | 5-10-10[a] | 122 | | 1.6 | 2.1 | 15.7 | 33.0 |
| 4806 | 4-12-8[a] | 100 | | 1.4 | 3.9 | 16.0 | 30.4 |
| 4413 | 5-10-5[b] | 95 | Adsorbed $H_2O$ | 5.3 | 11.5 | 29.5 | 38.0 |
| 443 | 6-8-4[c] | 60 | | 3.4 | 3.4 | 25.7 | 38.1 |
| 6199 | 8-8-8 | ... | | 10.2 | 18.6 | 30.4 | 40.8 |

[a] Nitrogen derived from nitrogen solution.
[b] Contained 90 pounds $NaNO_3$.
[c] Two units nitrogen derived from urea-ammonia liquor.

The last three samples in Table X are representative of the third class of mixtures that are hygroscopic due to a combination of materials incompatible with respect to moisture absorption. The 5-10-5 mixture, manufactured in New Jersey and containing 95 pounds ammonium nitrate and 90 pounds of sodium nitrate, had a satisfactory physical condition when it was mixed in February; but after bagging, it absorbed moisture to such an extent during the warm humid weather of May and June that it was unsatisfactory for use. The 6-8-4 mixture, manufactured in Louisiana, absorbs moisture in this area during storage in ordinary bags, as well as on the surface of the pile during bulk storage. While the composition of the 8-8-8 grade was not obtained, it was undesirably wet when sampled and undoubtedly contained incompatible materials as shown by the laboratory tests which place it among the most hygroscopic mixtures tested.

## CONCLUSIONS

To apply the results of this type of accelerated laboratory test in forecasting the relative amount of moisture absorption encountered under factory and field conditions, it is necessary to consider the prevailing temperature and humidity in the locality where the fertilizer is manufactured and used, as well as the moisture-resistant quality of the package in which the goods are sold. A relatively hygroscopic mixture, as measured by the accelerated test, may be manufactured and used satisfactorily in areas where the relative humidity is comparatively low. The same mixture, packed in moisture-resistant bags, may be satisfactory in more humid areas, provided it is used in a reasonably short time after the bags are opened.

Hygroscopicity is only one property of a fertilizer which affects its physical conditions. A nonhygroscopic mixture, as measured by the laboratory test, may absorb moisture to cause secondary curing and caking in the bag as a result of insufficient moisture content during the initial stages of manufacture. On the other hand, a nonhygroscopic mixture may become too damp in the storage pile as the result of an increase in volume of liquid phase through solution of a very soluble salt. An optimum amount of moisture in the fertilizer at mixing time is, therefore, highly important to the general physical condition of present-day mixtures containing very soluble hygroscopic materials.

ACKNOWLEDGMENT

Thanks are due to those members of fertilizer control stations, state experiment stations, and the fertilizer industry who kindly cooperated in furnishing samples and field data during the course of this study; also to W. H. Ross of this laboratory for many helpful suggestions.

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# Viscosity-Molecular Weight Relations for CELLULOSE ACETATE BUTYRATE

**J. W. TAMBLYN, D. R. MOREY, AND R. H. WAGNER**
*Eastman Kodak Company, Rochester, N. Y.*

**The relations between the molecular weights of fairly homogeneous fractions of cellulose acetate butyrate and the viscosity function $\ln \eta_r/c$ (determined in acetone and acetic acid) are given for the two cases: (*a*) the limiting value as $c \to 0$, known as intrinsic viscosity; (*b*) the value at $c = 0.25$ gram per 100 cc. The establishment of a relation using the latter viscosity figure permits the determination of the viscosity-average molecular weight without recourse to extrapolation to zero concentration. Upon degrading samples of heterogeneous (unfractionated) cellulose acetate butyrate by heat, ball milling, and ultraviolet, it was found that the $\ln \eta_r/c$ values and the number-average molecular weights (from osmotic pressure) are also related by equations similar in form to those obtained on fractions. A means is thus at hand for obtaining the more useful number average of heterogeneous cellulose acetate butyrate from a single viscosity measurement. It is pointed out that the establishment of a simple relation between these quantities for any polymer depends on the kinetics of the polymerization or degradation process and its effect on distribution curves.**

HIGH polymers are composed of mixtures of macromolecules of widely varying size. These heterogeneous mixtures can by a suitable procedure, be separated into a series of fractions, each of which is more homogeneous than the original material. Such a procedure, commonly called "fractionation", usually takes advantage of the dependence of solubility on molecular weight. Although it is impossible by this method to prepare fractions whose molecular weight distribution curves are very narrow or nonoverlapping, it is practicable to obtain fractions of sufficient homogeneity for many purposes.

The aim of this study has been: (1) To determine the relation 6) between intrinsic viscosity[1] and molecular weight for well-fractionated cellulose acetate butyrate fractions. Such a relation has been expressed for other polymer fractions in the form:

$$[\eta] = K \cdot {}^{n}\overline{M}^{a}$$

by Mark (*10*), Houwink (*4*), and Flory (*3*). (2) To determine whether an analogous relation between intrinsic viscosity and molecular weight exists for unfractionated samples of cellulose acetate butyrate which have been moderately degraded by heat, mechanical working, or ultraviolet light. Such a relation, if applicable to materials encountered commercially, would have considerable practical value because the number-average molecular weight of such heterogeneous samples would then be calculated from a single viscosity measurement.

The analytical definition of number-average molecular weight, ${}^{n}\overline{M}$, is:

$${}^{n}\overline{M} = \frac{\Sigma N_iM_i}{\Sigma N_i} = \frac{1}{\sum \frac{w_i}{M_i}}$$

where $N_i$ = number of molecules of weight $M_i$
$w_i$ = fraction by weight which these molecules constitute of the whole polymeric mixture

Other average molecular weights are given by Flory (*3*), Huggins (*5*), and Kraemer and Lansing (*7*). For example, weight-average molecular weight,

$${}^{w}\overline{M} = \frac{\Sigma N_iM_i^2}{\Sigma N_iM_i} = \Sigma w_iM_i$$

and viscosity-average molecular weight,

$${}^{v}\overline{M} = \left\{ \frac{\Sigma N_iM_i^{a+1}}{\Sigma N_iM_i} \right\}^{\frac{1}{a}} = \left\{ \Sigma w_iM_i^{a} \right\}^{\frac{1}{a}}$$

Spurlin (*13*) and Sookne and Harris (*12*) showed that the number-average molecular weight of cellulose derivatives is a better criterion of certain mechanical properties, such as fold resistance and extensibility, than is the viscosity-average molecular weight.

---

[1] According to Kraemer (*6*),

$$[\eta] = \frac{\ln \eta_r}{} \text{ as } c \to 0$$

The relative viscosity $\eta_r$ is taken to be the ratio of efflux time for solution to that for pure solvent, since the density is not significantly changed for the dilute solutions used.

TABLE I. FIRST FRACTIONATION OF CELLULOSE ACETATE BUTYRATE

| Fraction | Weight, Grams | [η] in Acetone at 25° C. | $^{n}\overline{M}$ | No. Grams Recombined to Form Groups | |
|---|---|---|---|---|---|
| Unfractionated original | 300 | 1.78 | 71,000 | .... | |
| 1 | 10.3 | 2.95 | 136,000 | 8.3 | |
| 2 | 3.3 | 2.90 | 130,000 | 2.0 | |
| 3 | 17.1 | 2.79 | ..... | 16.5 | A |
| 4 | 27.0 | 2.76 | ..... | 26.3 | |
| 5 | 12.3 | 2.40 | ..... | 11.8 | |
| 6 | 14.5 | 2.43 | 119,000 | 11.1 | |
| 7 | 18.0 | 2.40 | ..... | 17.3 | |
| 8 | 15.1 | 2.35 | ..... | 14.6 | B |
| 9 | 8.8 | 2.21 | ..... | 8.0 | |
| 10 | 9.7 | 2.12 | 107,000 | 6.4 | |
| 11 | 11.0 | 2.04 | ..... | 10.5 of No. 11 +<br>1.4 of No. 10 | |
| 12 | 10.5 | 1.93 | ..... | 10.0 | C |
| 13 | 12.3 | 1.72 | ..... | 11.9 | |
| 14 | 13.0 | 1.69 | 92,000 | 10.9 | |
| 15 | 15.1 | 1.54 | ..... | 14.5 | |
| 16 | 14.9 | 1.37 | 74,000 | 14.4 | |
| 17 | 14.9 | 1.32 | ..... | 14.4 | |
| 18 | 20.0 | 1.00 | 47,000 | 18.5 | D |
| 19 | 18.3 | 0.83 | ..... | 17.9 | |
| 20 | 8.6 | 0.53 | 29,000 | 7.0 | |
| 21 | 16.1 | 0.35 | ..... | 15.2 | |
| Total fractions | 290.8 | | | 268.9 | |
| Recovery, 97% | | | | | |

### FRACTIONATION PROCEDURE

In the fractionation of cellulose acetate butyrate (13.1% acetyl, 36.5% butyryl), a 2% acetone solution of the ester formed the initial solution. (Similar fractionations were carried out at concentrations of 1 and 0.05%, and no better separation was obtained.) To this was added a mixture of equal volumes of water and acetone, containing 2% of sodium chloride to aid coagulation of the precipitate. This precipitant mixture was added, with stirring, at 22° C. until a slight turbidity persisted. This suspension was dissolved by warming the flask a few degrees, and then allowing the flask to stand for 24 or more hours at 22° C. until the precipitate which formed on cooling had settled to the bottom. Most of the clear supernatant liquid was decanted and the remainder, containing the gel-like precipitated phase, was centrifuged. The separated gel was dissolved in acetone to make a dope of about 5% concentration, reprecipitated in fibrous form by running slowly into a large volume of water, washed with fresh water, filtered, dried, weighed, and labeled "fraction 1". Successive fractions were precipitated by additions of small volumes of water, containing about 2% of salt, and removed in the same way as fraction 1. The last fraction, the twenty-first, was obtained by evaporation of the solution to a point where practically no acetone remained. These fractions, which will be referred to as the first series of fractions, were measured and then recombined into four groups as shown in Table I. Each group was then refractionated by the procedure used for the first fractionation, and a second series of fractions was obtained whose properties are given in Table II.

**VISCOSITY DETERMINATION.** The intrinsic viscosities (*6*) given in these tables were obtained in an Ostwald capillary viscometer at 25° C. Measurements of the viscosity at concentrations of 0.125, 0.25, 0.5, and 1.0 gram per 100 cc. showed that the relation,

$$[\eta] = \frac{\ln \eta_r}{c}(1 + Bc)$$

could satisfactorily represent the data over the whole molecular-weight range covered by the fractions. Constant $B$ had the values 0.26 and 0.30 for acetone and acetic acid solutions, respectively. By means of these viscosity-concentration relations, the intrinsic viscosity can be obtained from a single viscosity measurement at a finite concentration below 1 gram per 100 cc.

**NUMBER-AVERAGE MOLECULAR WEIGHT DETERMINATION.** The osmotic pressures of the polymer solutions (in acetone at 25° C.) were measured in a modified Schulz osmometer (*14*), designed for operation by the static elevation method which involves the measurement of the height of liquid column or head after equilibration is complete. Corrections for surface tension were applied. The osmotic pressure, $\pi$, is related to concentration $c$ of the polymer by the equation (*5*):

$$\pi = \frac{RTc}{{}^{n}\overline{M}_p} + \frac{RT\,d_s(\frac{1}{2} - \mu)c^2}{M_s d_p^2} + \frac{RT\,d_s c^3}{3M_s d_p^3} \tag{1}$$

where subscripts $s$, $p$ = solvent and polymer, respectively
$d$ = density
$R$ = gas constant
$T$ = absolute temperature
$\mu$ = interaction factor described by Huggins

In the most unfavorable case of the systems reported here, the $c^3$ term of Equation 1 amounted to only 2% of $\pi$. Hence, it can be neglected without significant error and Equation 1 reduces to:

$$\frac{\pi}{c} = A + Bc \tag{2}$$

where

$$A = \frac{RT}{{}^{n}\overline{M}_p} \text{ and } B = \frac{RTd_s\,(\frac{1}{2} - \mu)}{M_s d_p^2}$$

By plotting $\pi/c$ as a function of $c$, the value of $A$ can be determined.

The semipermeable membrane used for these systems was of regenerated cellulose, kept in a wet and swollen condition from the time of its regeneration. It was further conditioned for use by the method previously described (*14*).

TABLE II. SECOND FRACTIONATION OF CELLULOSE ACETATE BUTYRATE

| Fraction | Weight, Grams | Ester Analysis, % | | [η] at 25° C. in: | | $^{n}M$ |
|---|---|---|---|---|---|---|
| | | Acetyl | Butyryl | Acetone | Acetic acid | |
| Unfractionated original | 268.9 | 13.1 | 36.5 | 1.78 | 1.97 | 71,000 |
| $A_1$ | 18.2 | 12.1 | 37.8 | 3.30 | 3.46 | 210,000 |
| $A_2$ | 13.9 | .. | .. | 3.19 | .. | 176,000 |
| $A_3$ | 11.1 | .. | .. | 2.90 | 3.08 | ..... |
| $A_4$ | 8.1 | .. | .. | 2.51 | .. | 148,000 |
| $A_5$ | 12.0 | .. | .. | 1.65 | .. | 83,000 |
| $A_6$ | 2.3 | .. | .. | 0.68 | .. | ..... |
| $B_1$ | 8.2 | .. | .. | 2.62 | .. | 136,000 |
| $B_2$ | 29.0 | 12.5 | 37.0 | 2.52 | 2.70 | ..... |
| $B_3$ | 5.0 | .. | .. | 2.22 | 2.38 | 122,000 |
| $B_4$ | 6.0 | .. | .. | 1.81 | .. | ..... |
| $B_5$ | 6.0 | .. | .. | 1.09 | .. | ..... |
| $B_6$ | 0.7 | .. | .. | 0.43 | .. | ..... |
| $C_1$ | 22.3 | .. | .. | 1.97 | 2.09 | 103,000 |
| $C_2$ | 29.4 | 12.9 | 36.7 | 1.76 | 1.94 | ..... |
| $C_3$ | 4.6 | .. | .. | 1.26 | 1.36 | ..... |
| $C_4$ | 3.3 | .. | .. | 0.77 | .. | 31,000 |
| $C_5$ | 0.5 | .. | .. | 0.28 | .. | ..... |
| $D_1$ | 16.7 | .. | .. | 1.23 | .. | 59,000 |
| $D_2$ | 17.7 | 12.8 | 36.6 | 1.09 | 1.19 | ..... |
| $D_3$ | 12.8 | .. | .. | 0.94 | 1.03 | ..... |
| $D_4$ | 13.7 | 13.2 | 36.4 | 0.77 | .. | ..... |
| $D_5$ | 15.1 | .. | .. | 0.51 | 0.53 | 20,000 |
| $D_6$ | 4.6 | .. | .. | 0.24 | 0.24 | 12,000 |
| Total fractions | 261.2 | | | | | |
| Recovery, 97% | | | | | | |

The external osmometer liquid, or dialyzate, was tested at the conclusion of each determination for the presence of high polymer by the evaporation of a portion of it to dryness. Polymers having number-average molecular weights of 30,000 or greater showed no evidence of a membrane-permeable component, at least not in sufficient quantity to exceed 0.1 mg. per 25 ml. of dialyzate. In only two of the determinations was the quantity of solute permeable to the membrane of serious concern; these were the lowest molecular-weight fractions $D_5$ and $D_6$ of Table II, of which about 2 and 5%, respectively, ultimately diffused through the membrane into the dialyzate. The rate of diffusion was rather slow, however, requiring 10 to 12 days and six changes of dialyzate to obtain essentially complete elimination of the diffusible polymer fraction.

A study of these diffusion rates made on cellulose acetate of about the same molecular weight as fractions $D_5$ and $D_6$ showed that the maximum pressure observed after the osmometer was assembled could be taken, to a very close approximation, as that corresponding to the sample in the absence of polymer diffusion.

We assumed, therefore, that the osmotic pressure molecular-weight values reported for fractions $D_5$ and $D_6$ have no significantly greater error than those of other fractions. All the experimental errors involved in the osmotically determined molecular weights result in an uncertainty of ±5% in the highest molecular weights and ±3% in the lower molecular weights.

## INFLUENCE OF POLYMER CHAIN FACTORS ON FRACTIONATION

The solubility characteristics of a polymer will depend on: solvent, type of chain, temperature, nature and number of side groups on the main chain, and length of chain. The separation into fractions is done in order to establish differences in length of chain. If, however, a significant separation takes place because of the nature and number of side groups, the purpose of the experiment is defeated.

It is known that in the partial esterification of cellulose there is a random placement of the side groups. Does this randomness cause one chain to differ from another in degree of esterification in a given esterification procedure? Table II gives the acetyl and butyryl analyses of some of the fractions. As the molecular weight decreases, the butyryl content also decreases and the acetyl value rises, while the total acyl content remains practically constant. These changes are quite small, approximately double the experimental error of a measurement. Any fractionation on a basis of acetyl-butyryl ratio is therefore minute compared with the fractionation which has taken place on a basis of chain length. These results are thus in agreement with those of other investigators (*9*) who found that a precipitation fractionation takes place on the basis of chain length. This may be further interpreted to mean that, for a fixed set of acylation conditions, the randomness of acylation of available hydroxy groups along a chain is on such a small scale that short chains do not differ from long chains in their average degree of acylation.

For a sample consisting of a mixture of batches, each of considerably different acyl content, a precipitation fractionation would separate on a basis of acyl content as well as chain length. This effect may account for the slight ester fractionation obtained here, since such commercial samples of cellulose esters are usually blends of a number of batches which are not exactly alike in ester content.

The relation between molecular weight and intrinsic viscosity was determined for each series of fractions by plotting $[\eta]$ against ${}^n\overline{M}$. Both series show about the same viscosity-molecular weight relation up to a molecular weight of approximately 100,000. Above this, there appears to be a significant difference between the two sets of fractions.

The following relation is found to hold for the double-fractionated material, using acetone at 25° C. as the solvent:

$$[\eta] = 13.7 \times 10^{-5}\, {}^n\overline{M}^{0.83} \tag{3}$$

Using acetic acid at 25° C., the relation is:

$$[\eta] = 14.6 \times 10^{-5}\, {}^n\overline{M}^{0.83} \tag{4}$$

These equations fit the data less well when the molecular weight takes on values below 20,000.

The quantity $[\eta]$, obtained by extrapolation of $\ln \eta_r/c$ to zero concentration, has more theoretical significance than a value of this viscosity function at some finite concentration. But for the practical purpose of obtaining a molecular weight average, a properly calibrated equation using a value of this function at a concentration of 0.25 gram of polymer per 100 cc. of solvent is equally as good, and has the advantage that the step of extrapolation, either by predetermined law or by additional data, is eliminated. Using the value of the function at a concentration of 0.25 gram per 100 cc., we obtain:

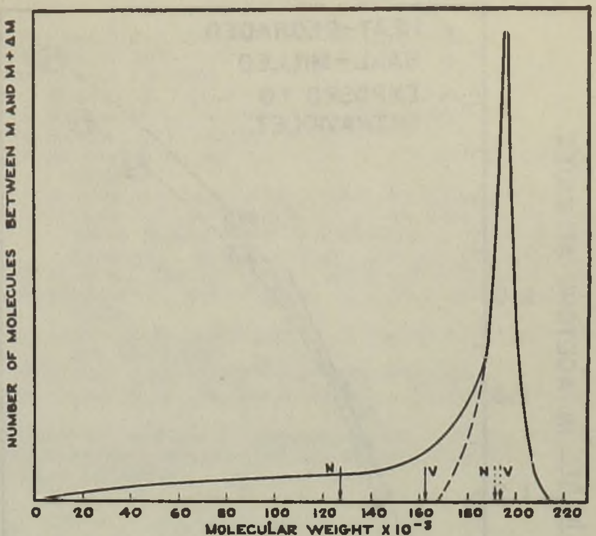

**Figure 1. Effect of Molecular Weight Distribution on Molecular Weight Averages**

**The unsymmetric curve is a smoothed distribution curve of the fractions which were combined to form group A of Table I. Such a (differential) curve is derived from the summation or integral distribution curve by plotting the slope of the latter against molecular weight. The summation curve is obtained by plotting as ordinate the gram weight percentage of material whose molecular weight exceeds a given value of *M* plotted as abscissa. The symmetrical peak curve, formed by the dashed line, merely represents a hypothetical narrow fraction which is used to show how closely the weight and number averages approach each other. A differential curve is quite sensitive to how the summation curve is made to pass through the experimental points.**

$$\text{Acetone at 25° C.:}\quad \frac{\ln \eta_r}{0.25} = 12.7 \times 10^{-5}\, {}^nM^{0.83} \tag{5}$$

$$\text{Acetic acid at 25° C.:}\quad \frac{\ln \eta_r}{0.25} = 13.5 \times 10^{-5}\, {}^n\overline{M}^{0.83} \tag{6}$$

$$\text{Pyridine at 25° C.:}\quad \frac{\ln \eta_r}{0.25} = 12.3 \times 10^{-5}\, {}^n\overline{M}^{0.83} \tag{7}$$

Routine usage of this quantity, $\ln \eta_r/0.25$, is facilitated by assigning to it a symbol and name. The word "intrinsic" is now, by established usage, associated only with the value at zero concentration and should therefore be avoided in this connection. As a suggestion, this quantity, which is related to the viscosity-average molecular weight of a polymer, could be called a "viscosity-average index" and denoted by $I_{0.25}$ for the particular concentration of 0.25 gram per 100 cc.

The more heterogeneous a material, the more do the number- and weight-averages differ from each other. Applying a relation obtained on fractions to an unfractionated material, the $M$ value obtained is a viscosity-average, which coincides in value with a number-average for the homogeneous fractions and deviates more and more therefrom for increasingly heterogeneous material. This is illustrated in Figure 1 where, for the symmetrical peak formed by the dashed line, the two averages $N$ and $V$ are nearly alike. For the unsymmetric full curve the calculated positions of the two averages are quite divergent, indeed the deviation of the ratio of these averages from unity is one measure of heterogeneity. (It is possible, however, to have curves of quite different shape and yet have the same ratio.) A further illustration of the divergence

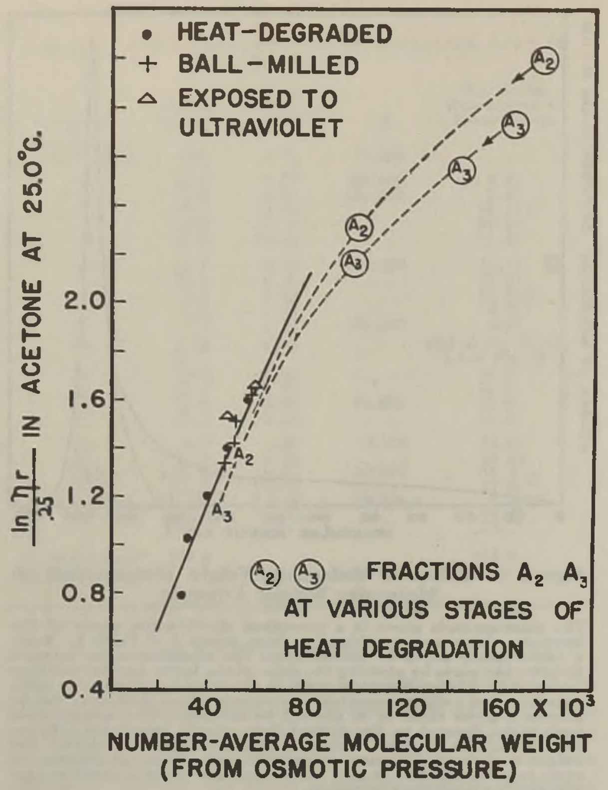

**Figure 2. Effect of Degradation on Homogeneity**

of the two averages is given in the following table where three samples, differing in heterogeneity but showing the same intrinsic viscosity, are compared:

| Material | ${}^{v}\overline{M}$ (from Viscosity) | ${}^{n}\overline{M}$ (from Osmotic Pressure) |
|---|---|---|
| Cellulose acetate butyrate fraction | 89,000 | 89,000 |
| Unfractionated original | 89,000 | 71,000 |
| Blend of fractions $A_2$ and $D_3$ (extreme heterogeneity) | 89,000 | 34,000 |

As a result of considerable labor of fractionation and from osmotic pressure and viscosity measurements, an empirical relation is obtained which yields, for unfractionated samples, a molecular weight averaged in a complex manner. A more fundamental and significant average is the number-average, and the desirable goal appears of deriving a number-average from a single viscosity measurement.

For types of distributions in which the ratio of weight- to number-averages remains constant, this goal is achieved immediately with the equation derived from fractions. Flory (*1*) showed that this condition is approximately true for linear condensation polyesters of high molecular weights.

If some new empirical relation can be found between measured viscosities and measured number-averages on a series of heterogeneous polymers, this shows that, even if the ratio of averages is not constant, it does not vary in a chance or erratic manner. Although the distribution curves of such a series of heteropolymers differ, they do so according to more fundamental kinetics of polymerization or degradation which imposes order on the ratio of the viscosity and number-averages.

A series of polyesters of ω-hydroxydecanoic acid studied by Kraemer and VanNatta (*8*) showed a definite relation between intrinsic viscosity and number average. These polymers were made in the hope of obtaining homogeneous samples, but it is apparent that the higher members, at least, were not homogeneous. Flory (*2*) concluded that these samples were not homogeneous.

Another example of relating the number-average of a heterogeneous polymer to a single viscosity measurement was given by Schulz and Dinglinger (*11*). For a heterogeneous polymethacrylate, an equation $[\eta] = K\,{}^{n}\overline{M} + b$ was derived in which $[\eta]$ and ${}^{n}\overline{M}$ refer to the unfractionated polymer.

Since in the processing of cellulosic plastic materials the molecular weights are always decreasing, it is of value to find out whether the degradation produced by heating, mechanical action, or ultraviolet light are of such a kinetic nature as to preserve regularity rather than randomness between the two averages. Therefore, samples of the original unfractionated cellulose acetate butyrate were moderately degraded by heat, by ball milling, and by ultraviolet light, as described in Table III.

It is found that a relation exists between the measured intrinsic viscosity and the number-average molecular weight; this relation is expressed reasonably well by

$$[\eta] = 18.5 \times 10^{-5}\,{}^{n}\overline{M}^{0.83} \tag{8}$$

$$\frac{\ln \eta_r}{0.25} = I_{0.25} = 17.7 \times 10^{-5}\,{}^{n}\overline{M}^{0.83} \tag{9}$$

The viscosities and osmotic pressures were measured in acetone at 25° C. The data of these experiments show larger errors, and there is a larger range of uncertainty in the selection of the proper exponent. Since the same value 0.83 falls within this range, we have adopted it as a tentative value for the case of heterogeneous samples also.

From Equation 9 and a single viscosity measurement, we may now calculate the number-average molecular weight of any sample of the unfractionated cellulose acetate butyrate which has been moderately degraded by heat, light, or mechanical action. Since this relation applies to materials encountered in practice, it should be of more practical use than equations relating to homogeneous fractions.

When degradation by heat or ultraviolet is carried too far, the polymers become partly insoluble in acetone. This indicates that some reaction other than simple degradation or chain breaking takes place to an important degree after long heating or irradiation Such excessively degraded products are not included in the data.

TABLE III. DEGRADATION OF CELLULOSE ACETATE BUTYRATE

| Starting Material | Treatment | In Acetone at 25° C. $[\eta]$ | In Acetone at 25° C. $\frac{\ln \eta_r}{0.25}$ | ${}^{n}\overline{M}$ |
|---|---|---|---|---|
| Unfractionated | None | 1.78 | 1.70 | 71,000 |
| | Heated in air | | | |
| | 150° C. for 14 hr. | 1.68 | 1.60 | 57,000 |
| | 150° C. for 48 hr. | 1.47 | 1.40 | 49,000 |
| | 155° C. for 19 hr. | 1.26 | 1.20 | 41,000 |
| | 175° C. for 2.5 hr. | 1.08 | 1.03 | 32,000 |
| | 175° C. for 5 hr. | 0.84 | 0.79 | 30,000 |
| | Ball-milled | | | |
| | 2 days | 1.70 | 1.62 | 58,000 |
| | 5 days | 1.60 | 1.52 | 52,000 |
| | 8 days | 1.49 | 1.42 | 52,000 |
| | 12 days | 1.41 | 1.34 | 48,000 |
| | Exposed to ultraviolet (G.E. S-4 lamp) | | | |
| | 8 hr. | 1.75 | 1.67 | 60,000 |
| | 24 hr. | 1.62 | 1.54 | 49,000 |
| Fraction $A_2$ | None | 3.24 | 3.00 | 176,000 |
| | Heated in air 160° C. | | | |
| | For 8 hr. | 2.46 | 2.32 | 102,000 |
| | For 17 hr. | 1.46 | 1.39 | 53,000 |
| Fraction $A_3$ | None | 2.92 | 2.73 | 164,000 |
| | Heated in air | | | |
| | 150° C. for 15 hr. | 2.73 | 2.56 | 144,000 |
| | 150° C. for 24 hr., 150–175° C. for 18 hr. | 2.30 | 2.18 | 100,000 |
| | 150° C. for 24 hr., 150–175° C. for 28 hr. | 1.18 | 1.13 | 44,000 |

There is some indication that the products degraded by ultraviolet light follow a law such as Equation 9 but with constants differing from those of heat or mechanically degraded products. However, more data are needed to establish this point.

A marked example of the effect of degradation upon homogeneity is illustrated in Figure 2. Degradation of homogeneous fractions $A_2$ and $A_3$ shows that, as degradation progresses, they move to the left of their original line as defined by Equation 5 and approach the heterogeneity of the other degraded samples. This is shown by the dashed lines of Figure 2.

It is by no means evident that for other heteropolymers, in a series corresponding to stages of processing, a definite relation can be found between a viscosity function and the number-average. The usefulness of such a relation justifies a search for it.

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# Iron Pentacarbonyl as Antiknock Agent in Alcohol Motor Fuels

**ISADORE PITESKY and RICHARD WIEBE**
*Northern Regional Research Laboratory*
*U. S. Department of Agriculture, Peoria, Ill.*

IN CONNECTION with work on knock suppressors for agricultural motor fuels, an investigation was made of iron pentacarbonyl, since it is an excellent antiknock agent for ethyl alcohol. The term "ethyl alcohol" is used here in the chemical sense and is equivalent to anhydrous ethyl alcohol. Tetraethyllead is not only totally ineffective in ethyl alcohol but actually depresses the octane rating. That the two metallic compounds, tetraethyllead and iron pentacarbonyl, both extremely effective in gasoline, should have diametrically opposite effects in ethyl alcohol is somewhat surprising. Since this laboratory is interested in the development of motor fuels derivable from agricultural products, it was considered desirable to obtain any pertinent information. The purpose of this paper is to present experimental data concerning its action on alcohol motor fuels.

In these tests a commercial product better than 99% pure was used which was further purified by repeated distillations either in vacuo or in a countercurrent of nitrogen. All operations were carried out either in the dark or in red illumination. The physical and chemical properties were described by Blanchard and others (*2*, *4*, *12*, *13*, *14*).

### ENGINE TESTS

Knock ratings were made according to the A.S.T.M. Tentative Method of Test for Knock Characteristics of Motor Fuels (D357-43T). Tables I and II give some of the results obtained.

Two difficulties were encountered in rating fuels containing iron pentacarbonyl, and therefore the highest accuracy cannot be claimed for the data. Usually after a few runs the knockmeter readings became erratic because of a deposit of iron oxide on the diaphragm of the bouncing pin. This was partially overcome by making only three to five octane number determinations before overhauling the engine. The other difficulty was the persistence of action of iron pentacarbonyl in the engine, probably because of an active deposit of iron oxide on the cylinder walls which

**Iron pentacarbonyl is an effective antiknock agent for ethyl alcohol fuels; however, caution must be observed when it is used in motor fuels, since the iron oxide deposit may seriously interfere with engine operation. The action of light changes iron pentacarbonyl to iron enneacarbonyl which is practically insoluble in hydrocarbon fuels. Iron enneacarbonyl, however, is soluble in ethyl alcohol, at least to the extent tested, and no obnoxious precipitate occurs in this fuel. Small amounts of oleic, palmitic, and stearic acids and of triethanolamine oleate are effective stabilizers for the iron pentacarbonyl in some hydrocarbon fuels; however, no generalization can be made at present. For solutions in anhydrous ethyl alcohol and in ethyl alcohol containing 5% water by volume, no stabilizer is necessary. If reasonable precautions are observed, working iron pentacarbonyl is probably no more dangerous from a health standpoint than tetraethyllead.**

affected, at least for a time, the octane number of the reference fuels. This factor was variable, and the extent of its influence on the data would depend to some extent on the operator's judgment.

A comparison of Tables I and II shows the significant differences between the action of iron pentacarbonyl and tetraethyllead on ethyl alcohol as a fuel. While 0.25% by volume of iron pentacarbonyl will raise the octane number from 90 to 99, 1 ml. of tetraethyllead depresses the rating to 85; further amounts of lead up to 3 ml. have no effect.

TABLE I. IRON PENTACARBONYL SUSCEPTIBILITY OF FUELS EXPRESSED AS OCTANE NUMBERS

| Fuel | $Fe(CO)_5$ Added, % by Vol. (Ml./Gal.) 0 | 0.1 (3.8) | 0.25 (9.5) |
|---|---|---|---|
| Ethyl alcohol | 90 | 95 | 99 |
| 75% ethyl alcohol + 25% benzene | 91 | 93 | |
| 50% ethyl alcohol + 50% acetone | 100 | 0.06 ml.[a] | 0.24 ml.[a] |
| 90% 90 octane + 10% alcohol | 91 | 0.09 ml.[a] | 0.24 ml.[a] |
| 80% 90 octane + 20% alcohol | 92 | 0.09 ml.[a] | 0.24 ml.[a] |
| 90% ethyl alcohol + 10% $H_2O$ | 97 | 0.11 ml.[a] | |
| Reference gasoline (75.7 F-4 in C-13)[b] | 90 | 96 | 0.24 ml.[a] |

[a] When the knock value of the fuel is greater than that of iso-octane, it is expressed in terms of iso-octane + milliliters of tetraethyllead.

[b] Octane number of F-4 is 99 and that of C-13 is 71.2.

Iron pentacarbonyl seems to have a slightly higher antiknock influence on gasoline than on alcohol, at least in the case of the reference fuel noted. The effect of lead on gasoline is considerably greater.

In fuels containing stabilizers, iron enneacarbonyl might exist in molecular aggregates rather than in single units, and since it is known that the state of subdivision of an antiknock is important, it is conceivable that such solutions would show a decrease in octane rating. Any nonvolatile antiknock agent will also be partially lost in a carburetor engine; however, this loss may be very small.

TABLE II. LEAD SUSCEPTIBILITY OF FUELS EXPRESSED AS OCTANE NUMBERS

| Fuel | Tetraethyllead, Ml./Gal. 0 | 1 | 2 | 3 |
|---|---|---|---|---|
| Ethyl alcohol | 90[a] | 85 | 85 | 85 |
| Ethyl alcohol + 2 ml. $Fe(CO)_5$/gal. | 93[b] | 91 | 89 | .. |
| 90% ethyl alcohol + 10% aniline | 96 | 91 | .. | 91 |
| Reference gasoline (75.7 F-4 in C-13)[c] | 90 | 98 | 0.09 ml.[d] | .. |

[a] The octane number of ethyl alcohol has been variously reported from 90 to 99; however, we believe the correct value lies between 90 and 91.

[b] Interpolated value.

[c] See Table I, footnote [b].

[d] See Table I, footnote [a].

In order to obtain a rough idea regarding the effect or iron oxide deposit within the engine during operation, tests were run in a Lauson RLC 152, 1/2 to 3/4 horsepower, single-cylinder, air-cooled engine, using a fuel consisting of 0.1% by volume of iron pentacarbonyl in ethyl alcohol. The engine stopped after 78 hours because deposits on the exhaust valve seat prevented compression; it is suggested that since sleeve valve engines have less lead trouble, they may also be more suitable for use with fuels containing iron pentacarbonyl. After the initial soft film of iron oxide had been deposited on the walls, there seemed to be no tendency for the amount of deposit to increase. Tests also included additions of small amounts (0.1 to 1%) of butyl borate which is reported to make the iron oxide film nonconductive through possible formation of iron monoboride and in general to have a "favorable influence" (*9*). Under the condition of the experiment no such advantage was found. It must be emphasized that the work was done with only one type of engine, which may have been particularly unsuited for fuels containing carbonyl. Tests extending over two years (*8*) have shown that iron pentacarbonyl can, apparently without detriment, be used as antiknock in fuels; however, its use has been practically discontinued. Harrington (*6*) mentioned the fact that iron pentacarbonyl is being sold as an antiknock under the trade name "Ferroline". Another instance of its use in motor fuels has also come to the attention of the authors.

## STABILITY TESTS

Iron pentacarbonyl, alone and in dilute solution, is very unstable towards blue light and changes to iron enneacarbonyl (diferrononacarbonyl) and carbon monoxide according to the following equation:

$$2Fe(CO)_5 = Fe_2(CO)_9 + CO$$

The rate of formation of iron enneacarbonyl is a function of light intensity and will proceed rapidly in direct sunlight. In the case of a 0.1% solution of iron pentacarbonyl in iso-octane, for example, the above reaction is indicated first by a deepening of color, followed by the appearance of a precipitate of golden-yellow to orange-colored thin plates of iron enneacarbonyl, since the latter compound is practically insoluble in hydrocarbons. Iron enneacarbonyl is partially soluble in ethyl alcohol, and an identical solution of iron pentacarbonyl in this solvent will, on exposure to light, show only a gradual change from very pale yellow to dark orange, no precipitate being formed. In the absence of air such a solution will remain stable; however, if it is fully exposed to air, dissolved oxygen may gradually react with the dissolved enneacarbonyl and give rise to a finely divided precipitate of ferric oxide or hydroxide.

Leahy (*11*) not only made an extensive survey of the literature but also performed some experiments with certain stabilizing agents for the purpose of preventing the formation of iron enneacarbonyl. (The word "stabilizer", as used in this article, refers to a substance which, presumably through peptization or otherwise, prevents the precipitation of iron enneacarbonyl.) He claimed some success but does not disclose the nature of the substances he used. It was impossible to test the many claims made in various patents and articles, and no attempt, therefore, was made to cover the field. Many substances were tested, but the results obtained in only a few typical cases are given in Table III. Twelve samples of each of the various stabilizers were observed over a period of two weeks. Six of the samples were kept in the dark, and six were exposed to light except where otherwise stated. Three of each of the two sets were open to the atmosphere: the other three were kept in tight-stoppered test tubes. No difference was observed between the samples in stoppered and in open containers. The time recorded in Table III gives the interval which elapsed before a precipitate was observed. Samples were exposed to light from the north during August. All solutions remained stable in the dark. None of the substances tested was found to inhibit the action of light, although several were effective in preventing the precipitation of iron enneacarbonyl for the duration of the test.

Since, as previously mentioned, enneacarbonyl is soluble in ethyl alcohol, at least to the extent of its equilibrium concentration present in fuels, no precipitate was formed, and only a darkening of the solution was observed. The solubility of enneacarbonyl in ethyl alcohol decreased with increasing water content, and measurements are now in progress in this laboratory to determine the solubility of iron enneacarbonyl in various solvents. Solutions of pentacarbonyl in leaded gasoline appear to be slightly more stable, although no reason can be given. Palmitic acid, stearic acid, and triethanolamine oleate appear to be good stabilizers; however, the behavior of commercial iso-octane and particularly that of ethyl alcohol show that no generalization should be made. It was also observed that the purity of the reagents—e.g., triethanolamine oleate—was important, and that excess of either oleic acid or triethanol amine caused the formation of a precipitate in ethyl alcohol. Basic solutions of iron pentacarbonyl are very susceptible to oxidation, and it was found that additions of 0.001% of formic or acetic acid to ethyl alcohol prevent any possible formation of ferric hydroxide.

Bowen and Tietz (*3*) observed the effect of small quantities of various antiknock substances on the photochemical oxidation of acetaldehyde. Both iron and nickel carbonyl inhibited the reaction; tetraethyllead had no effect on the reaction rate. In the case of iron pentacarbonyl, inhibition was proportional to the amount added, and the reaction proceeded normally after the close of the induction period. The results with nickel carbonyl, however, were inconclusive, since the amount added was so large as to inhibit the reaction completely, and no induction period was observed. The strikingly different behavior of iron and lead in this reaction might give some clue regarding their equally different behavior in alcohol fuels, particularly since acetaldehyde has been shown to influence the ignition temperature–pressure relation of ethyl alcohol–air mixtures (*10*).

Egerton and Gates (*5*) found that, although tetraethyllead raised the self-igniting temperatures of various hydrocarbon fuels, as well as of acetaldehyde, normal alcohols were little affected. This, incidentally, was true also for benzene which, in actual operation, shows a low to zero lead susceptibility. All that can be said at present is that lead and iron compounds in ethyl alcohol show a distinct difference of behavior both in the laboratory as well as in the engine; however, experimental evidence, such as the addition of 10% of acetaldehyde without effect on the knock rating, is too contradictory. In order to maintain existing theories of intermediate compounds—e.g., the formation of peroxides—recourse must be had to assumptions which cannot or have not yet been verified.

To illustrate that precautions must be observed when working with pure iron pentacarbonyl, one incident should be recorded: After filtering a residual amount of iron pentacarbonyl which had been left in a shipping container to separate the enneacarbonyl formed, the filter paper with precipitate was left in the funnel under a hood. After a time a dull sound was heard; investigation showed that the enneacarbonyl had been oxidized to iron oxide apparently with somewhat explosive violence. Both Mittasch (*13*) and Blanchard (*2*) mentioned this reaction but are not in total agreement as to its cause. Mittasch states that iron enneacarbonyl is very sensitive to atmospheric oxygen and will ignite when rapidly dried; Blanchard found that the enneacarbonyl is very stable in dry air but, when moistened with iron pentacarbonyl, may ignite spontaneously. Either explanation was applicable in this case, and no attempt was made to investigate the real cause.

TABLE III. EFFECT OF STABILIZERS ON FUELS CONTAINING 0.1% BY VOLUME OF IRON PENTACARBONYL

(The time given is that required for the formation of a precipitate of iron enneacarbonyl)

| Fuel | Control | | 0.1% Oleic Acid (*7*) | | 0.1% Palmitic Acid (*7*) | | 0.1% Stearic Acid (*7*) | |
|---|---|---|---|---|---|---|---|---|
| | Dark | Light | Dark | Light | Dark | Light | Dark | Light |
| Ethyl alcohol | No change | Clear brown[a], no ppt. | No change | Turbidity in 15 min.; heavy ppt. in 2 hr. | No change | Turbidity in 15 min.; heavy ppt. in 2 hr. | No change | Turbidity in 15 min.; heavy ppt. in 2 hr. |
| Ethyl alcohol + 5% $H_2O$ | No change | Same | No change | Same | No change | Same | No change | Same |
| Ethyl alcohol + 10% $H_2O$ | No change | Slight turbidity in 1 hr.[b], no ppt. | No change | Same | No change | Same | No change | Same |
| Benzene, thiophene-free | No change | 3 hr. | No change | Clear brown, no ppt. | No change | Clear brown, no ppt. | No change | Clear brown, no ppt. |
| Gasoline, V-80 leaded | No change | 2 days | No change | Same | No change | Same | No change | Same |
| Iso-octane, commercial | No change | 3 hr. | No change | Same | No change | 2–3 days | No change | 2–3 days |
| Reference fuel, M-3 | No change | 3 hr. | No change | Same | No change | Clear brown, no ppt. | No change | Clear brown, no ppt. |
| Reference fuel, A-6 | No change | 3 hr. | No change | Same | No change | Same | No change | Same |
| Reference fuel, C-13 | No change | 3 hr. | No change | Same | No change | Same | No change | Same |
| Skellysolve C | No change | 3 hr. | No change | Same | No change | Same | No change | Same |

| Fuel | 0.1% Ammonium Oleate (*7*) | | 0.1% Triethanolamine Oleate (*7*) | | 1,4-*p*-Toluidoanthraquinone, 0.01% (*1*) | | Oil Brown Dye (*1*), 0.01% | |
|---|---|---|---|---|---|---|---|---|
| | Dark | Light | Dark | Light | Dark | Light | Dark | Light |
| Ethyl alcohol | No change | Turbidity in 15 min.; heavy ppt. in 2 hr. | No change | Clear brown, no ppt. | No change | No change[c] | No change | Deeper brown, no ppt. |
| Ethyl alcohol + 5% $H_2O$ | No change | Same | No change | Same | No change | No change[c] | No change | Same |
| Ethyl alcohol + 10% $H_2O$ | No change | Same | No change | Same | No change | No change[c] | No change | Turbidity, ppt. in 2 min. |
| Benzene, thiophene-free | No change | 2 days | No change | Same | No change | 2 hr. | No change | 4 hr. |
| Gasoline, V-80 leaded | No change | 6 days | No change | Same | No change | 3 days | No change | 2 days |
| Iso-octane, commercial | No change | 2 days | No change | Same | No change | 2 hr. | No change | 4 hr. |
| Reference fuel, M-3 | No change | 2 days | No change | Same | No change | 2 hr. | No change | 4 hr. |
| Reference fuel, A-6 | No change | 2 days | No change | Same | No change | 2 hr. | No change | 4 hr. |
| Reference fuel, C-13 | No change | 2 days | No change | Same | No change | 2 hr. | No change | 4 hr. |
| Skellysolve C | No change | 2 days | No change | Same | No change | 2 hr. | No change | 4 hr. |

[a] These tests were carried on for one month.
[b] Became opalescent within 1 hour, but no precipitate formed.
[c] Color change, if any, masked by dye; color remained green.

## ACKNOWLEDGMENT

The writers wish to thank C. F. Elder and F. R. Truby for conducting the engine tests, and C. B. Kretschmer for help in the preparation of iron pentacarbonyl.

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# EFFECT OF TEMPERATURE ON STRENGTH OF LAMINATES

**PATRICK NORELLI AND W. H. GARD**

*Westinghouse Electric & Manufacturing Company, East Pittsburgh, Pa.*

**This paper deals with the specialized field of phenolic laminates, and reports their tensile, compressive, and shear characteristics from −55° to 200° C. The elevated temperatures were attained by means of a small cylindrical furnace constructed to employ electrical resistance heating. To reach subnormal temperatures, a bath of solid carbon dioxide and alcohol was employed in a cylindrical vessel of annular construction. The yield strength, ultimate strength, modulus of elasticity intension, ultimate strength in compression, ultimate strength in shear are reported at −55°, −20°, 0°, 25°, 75°, 150°, and 200° C. We may conclude from the results that the tensile, compressive, and shear strengths of phenolic laminates are inversely proportional to temperature, and that the cellulose-filled materials are more sensitive to temperature change than their mineral-filled counterparts. The rate of loss of strength as a function of temperature increases above room temperature for the cellulose-filled laminates, whereas it decreases for the mineral-filled materials. Evidence of this variable change is supported by thermal expansion data for a typical laminate. The thermal expansion curve is shown to have a transition point at a temperature well within the range at which the accelerated change in physical properties seems to take place.**

PROPER use of plastic laminates requires a knowledge of their physical properties over the range of temperatures at which the product might be employed. This paper deals with this problem in the field of commercial phenolic laminates; one melamine laminate is included. The test program has not yet been completed; therefore, this article reports only the tensile, compressive, and shear characteristics of various types of laminates from −55° to 200° C. The minimum temperature in this range is a practical one; laminates have been used at a much lower temperature. The maximum temperature employed in these tests is higher than that normally recommended for laminates. Phenolic laminates can be used continuously at 100° to 125° C. and intermittently at 150° to 175° C.

Five test specimens were employed at each temperature for each test. The materials constitute a representative cross section of those generally used in the mechanical grades of phenolic laminates. The samples were obtained from regular production-line boards or sheets. A commercial type of cresylic acid resin was used in their manufacture. A description of the grades utilized follows:

| Materia Designation | NEMA or ASTM Grade | Filler | Resin, % |
|---|---|---|---|
| A | C | Coarse-weave cotton fabric | Phenolic, 35–40 |
| B | X | Kraft paper | Phenolic, 40–45 |
| C | AA | Asbestos cloth | Phenolic, 40–45 |
| D | XX | Alpha paper | Phenolic, 50–55 |
| E | LE | Fine-weave cotton fabric | Phenolic, 50–55 |
| F | (Exptl.) | Fiberglas fabric | Phenolic, 35–40 |
| G | AA | Asbestos fabric | Melamine, 40–45 |

## TEST METHODS

GENERAL. A standard Amsler 30-ton test machine was employed for all tests. This machine has a maximum head speed at no load of 0.050 inch per minute. The elevated temperatures were attained by a small cylindrical furnace constructed to employ electrical resistance heating

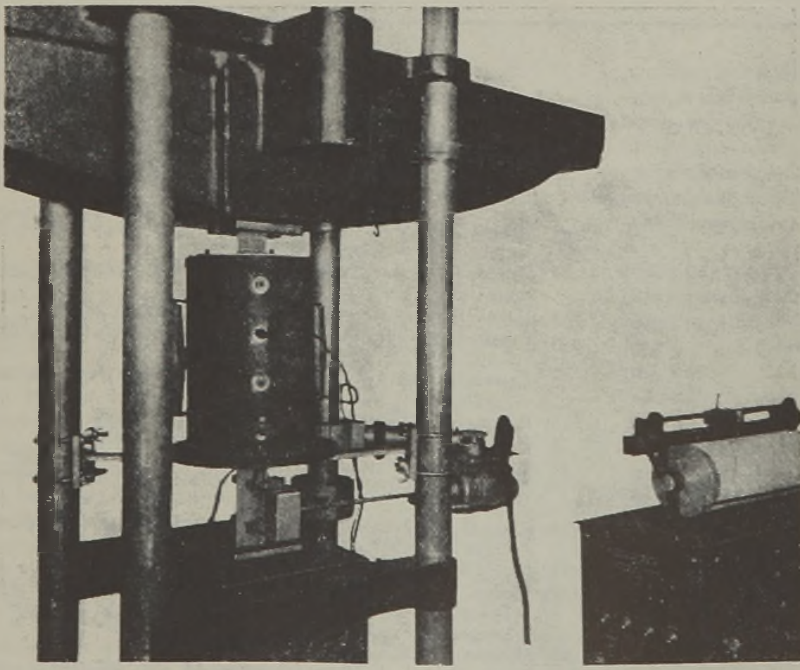

Figure 1. Apparatus for Tensile Testing

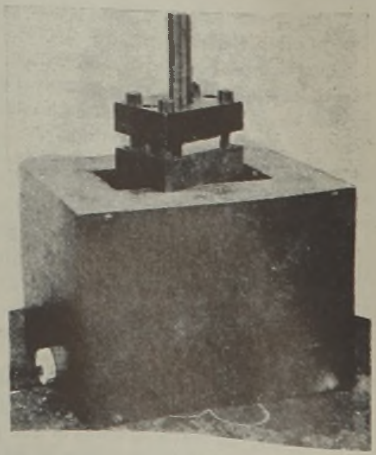

Figure 2. Equipment for Shear Tests

with variable voltage input. To attain subnormal temperatures a bath of solid carbon dioxide and alcohol was used in a cylindrical vessel of annular construction. An experienced operator can control the lower temperatures within 2° C. by the proper amount of dry ice. Figure 1 shows the setup for the tensile tests, and Figure 2 shows the shear test setup.

The test specimen was mounted in the machine with the heating or cooling chamber in place and the temperature adjusted. The temperature was measured by a thermocouple fastened to the test specimen (Figure 3). The time required to attain thermal equilibrium for the various temperatures was as follows:

| Temp., ° C. | Equilibrium Time, Hr. | Temp., ° C. | Equilibrium Time, Hr. |
|---|---|---|---|
| −55 | 5–6 | 75 | 2 |
| −20 | 3 | 150 | 3 |
| 0 | 2 | 200 | 5 |
| 25 | ... | ... | .. |

No attempt was made to precondition the test specimens; they were tested as received. While it is admitted that the time required to attain thermal equilibrium does affect the test specimens (and the effect is detrimental at the higher temperature), this procedure was followed because it was practical.

Table I. Average Values of Tensile Properties (in Pounds per Square Inch)

| Type | −55° C. | −20° C. | 0° C. | 25° C.[a] | 75° C. | 150° C. | 200° C. |
|---|---|---|---|---|---|---|---|
| | | | *A.* Ultimate Tensile Strength | | | | |
| A | 10,350 | 9,770 | 9,290 | 8,720 | 5,310 | 3,530 | 1,200 |
| B | 21,570 | 22,060 | 22,880 | 22,700 | 11,530 | .... | .... |
| C | 11,750 | 10,530 | 10,000 | 9,380 | 8,890 | 7,940 | 7,320 |
| D | 15,520 | 14,930 | 13,920 | 12,250 | 7,720 | .... | .... |
| E | 14,830 | 13,700 | 12,700 | 12,330 | 7,340 | .... | .... |
| F | 51,420 | 44,350 | 42,540 | 37,500 | 31,460 | 29,260 | 29,220 |
| G | 12,990 | 12,290 | 11,460 | 10,350 | 9,220 | 8,310 | 5,930 |
| | | | *B.* 0.2% Yield Strength in Tension | | | | |
| A | 6,640 | 6,780 | 7,290 | 5,200 | 3,050 | 1,575 | 1,300 |
| B | .... | .... | .... | 16,000 | 8,200 | .... | .... |
| C | 10,060 | 9,045 | 8,810 | 7,720 | 6,290 | 4,440 | 3,380 |
| D | 11,840 | 11,010 | 10,140 | 8,480 | 6,240 | .... | .... |
| E | 13,835 | 10,110 | 9,960 | 7,200 | 4,610 | .... | .... |
| F | 30,860 | 28,600 | 30,450 | 28,600 | 25,750 | 4,945 | 4,760 |
| G | 10,540 | 8,520 | 8,090 | 8,040 | 6,740 | 6,590 | 4,600 |
| | | | *C.* Modulus of Elasticity in Tension (× $10^6$) | | | | |
| A | 1.15 | 0.99 | 0.99 | 0.87 | 0.51 | 0.38 | 0.22 |
| B | 2.37 | 2.15 | 1.95 | 2.08 | 1.39 | .... | .... |
| C | 2.10 | 2.0 | 1.84 | 1.95 | 1.37 | 1.1 | 0.70 |
| D | 2.19 | 1.5 | 1.4 | 1.2 | 0.85 | .... | .... |
| E | 1.52 | 1.4 | 1.3 | 1.2 | 0.65 | .... | .... |
| F | 2.8[b] | 3.1 | 3.3 | 2.9 | 2.8 | 2.6 | 2.2 |
| G | 4 | 3.7 | 3.5 | 2.0 | 1.5 | 1.0 | 1.3 |

[a] Room temperature.
[b] at − 46° C.

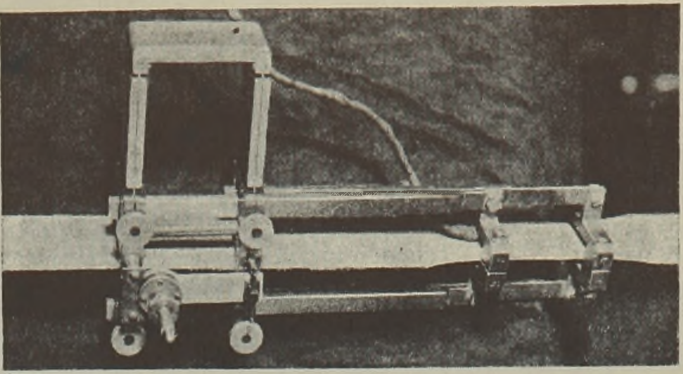

Figure 3. Method of Fastening Thermocouple to Test Specimen

TENSION. The stress-strain curves were obtained with a Baldwin-Southwark recorder. Figure 3 shows the method of clamping the extensometer to the test specimen. The ends of each tensile test specimen were always scored and sandpapered to minimize slippage in the grips of the machine. The tensile test specimens were shaped according to the A.S.T.M. standards on plastics and were approximately $^1/_4$ inch thick; they were a little longer ($19^1/_2$ inches) than usual to keep the grips of the testing machine out of the heating or cooling chamber.

COMPRESSION. The compression test samples were approximately one-inch cubes cut from one-inch-thick laminated boards. The heating and cooling chambers employed for the tensile tests were also used for the compressive tests.

SHEAR. Several shear fixtures were tried before it was decided to use the punch and die type which is under consideration for approval by A.S.T.M. Committee D-20 on plastics. A cross-sectional view of the shear test fixture is given in Figure 4. A phenolic laminate shear fixture was made for use at the lower temperatures. Its insulating properties shortened the time required to reach and maintain these lower temperatures. A tool steel fixture was made for use at elevated temperatures. The punch and die type of shear fixture was employed because it seemed to minimize bending of the specimen during the test. All shear test specimens were $^1/_2$ inch thick.

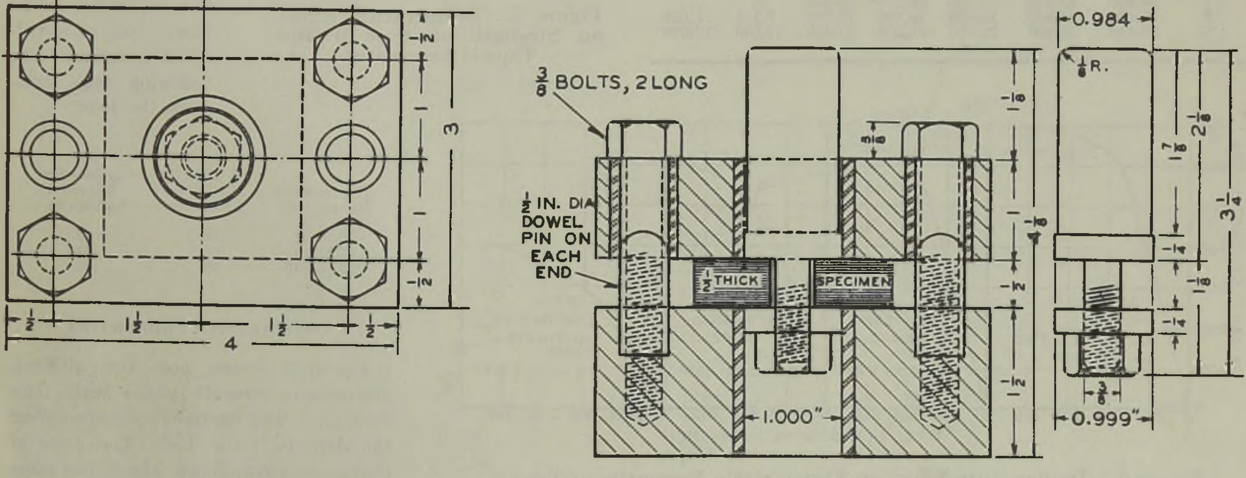

Figure 4. Proposed A.S.T.M. Shear Tool (Punch Type) for 0.010 to 0.500 Inch

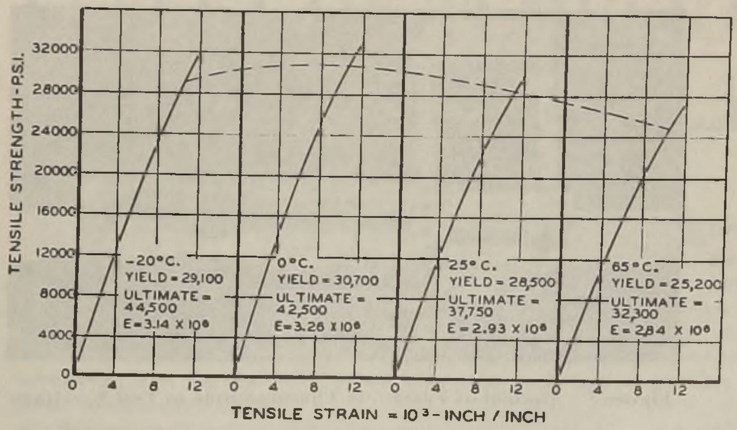

**Figure 5. Stress-Strain Curves at Various Temperatures for Type A Laminate**

### DEFINITIONS

The yield strength in tension was determined by drawing a line parallel to the initial straight-line portion of the curve and at an offset of 0.002 inch per inch. The stress which corresponds to the intersection of this line with the stress-strain curve is arbitrarily defined as the yield strength.

The modulus of elasticity in tension is taken as the ratio of stress over strain (stress/strain) for any point on the straight-line portion of the stress-strain curve.

The ultimate compressive strength is defined as the ultimate compressive load divided by the original bearing area of the test specimen.

Table II. Ultimate Compressive Strengths (in Pounds per Square Inch)

| Type | −55° C. | −20° C. | 0° C. | 25° C. | 75° C. | 150° C. | 200° C. |
|---|---|---|---|---|---|---|---|
| | | | *A.* Flatwise Direction | | | | |
| A | 51,000 | 44,930 | 42,500 | 42,120 | 29,850 | 19,460 | 11,600 |
| B | 48,800 | 44,800 | 41,800 | 44,030 | 33,530 | .... | .... |
| C | 54,960 | 48,700 | 43,630 | 48,550 | 38,430 | 25,300 | 30,780 |
| D | 54,100 | 48,250 | 44,630 | 39,950 | 29,150 | .... | .... |
| E | 54,100 | 45,300 | 43,900 | 43,200 | 31,730 | .... | .... |
| F | 73,200 | 66,900 | 47,400 | 69,750 | 48,870 | 35,130 | 23,700 |
| G | 51,820 | 47,530 | 41,800 | 46,800 | 37,660 | 27,160 | 38,500 |
| | | | *B.* Edgewise Direction | | | | |
| A | 37,350 | 30,300 | 27,050 | 24,250 | 15,550 | 9,825 | 8,600 |
| B | 33,400 | 30,450 | 26,750 | 26,075 | 16,750 | .... | .... |
| C | 22,250 | 22,450 | 19,800 | 20,575 | 15,225 | 12,620 | 11.675 |
| D | 38,300 | 30.800 | 29,700 | 25,700 | 15.975 | .... | .... |
| E | 39,850 | 33,900 | 33,100 | 27,900 | 19,900 | .... | .... |
| F | 20,400 | 14,800 | 18,830 | 14,195 | 13,700 | 7,325 | 7,025 |
| G | 23,450 | 23,300 | 22,100 | 21,000 | 21,400 | 11,095 | 12,070 |

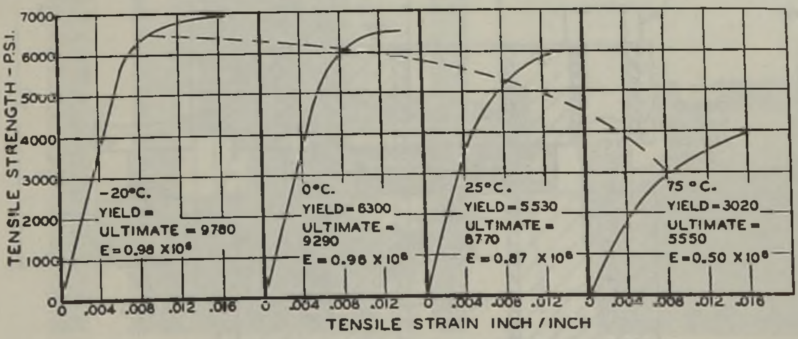

**Figure 6. Temperature Effect on Stress-Strain Properties of Type F Laminate**

The ultimate shear strength was determined by dividing the load (in pounds) by the area of the shear edge which is taken as the product of the thickness of the specimen by the circumference of the punch.

### TENSILE PROPERTIES

The ultimate tensile strengths are listed in Table 1*A*; the yield strength at 0.2% offset is given in Table I*B* with the exception of material B (kraft paper filler), which does not seem to have such a point except at the most elevated temperatures. The stress-strain curve for material B is a straight line up to its breaking point. Table I*C* contains values of modulus of elasticity in tension which were calculated from the straight-line portion of the stress-strain curves.

Figures 5 and 6 illustrate the stress-strain diagram for specific materials at four temperatures. Each curve represents an actual test taken from approximately the middle of the range for the samples tested; that is, the specimens represented by these curves have approximately the average tensile properties shown in Table I. The yield points for each material are connected by a dotted line to show its variation with temperature. Comparison of the slopes of the straight-line portion of these curves shows how the elastic modulus in tension decreases with increasing temperature.

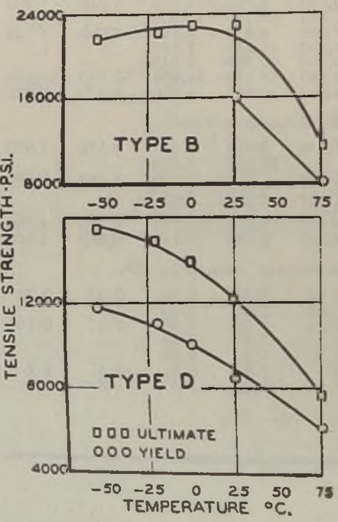

**Figure 7. Temperature Effect on Strength of Type B and Type D Laminates**

Figures 7 and 8 show the effect of temperature on the ultimate and yield strengths of specific materials. The percentage change in strength is greater for cellulose-filled than for mineral-filled plastics. The following table compares the two:

| Temperature Range, ° C. | % Loss for Cellulose Laminates | % Loss for Mineral Laminates |
|---|---|---|
| −55 to 25 | 13.5 | 22 |
| −55 to 75 | 48.7 | 31 |
| −55 to 200 | 88 | 45 |

### COMPRESSIVE PROPERTIES

Figure 9 shows how the ultimate compressive strength varies with temperature. The curves were drawn from the data in Table II*A*. The rates of change in strength are about the same except for asbestos-filled laminates C and

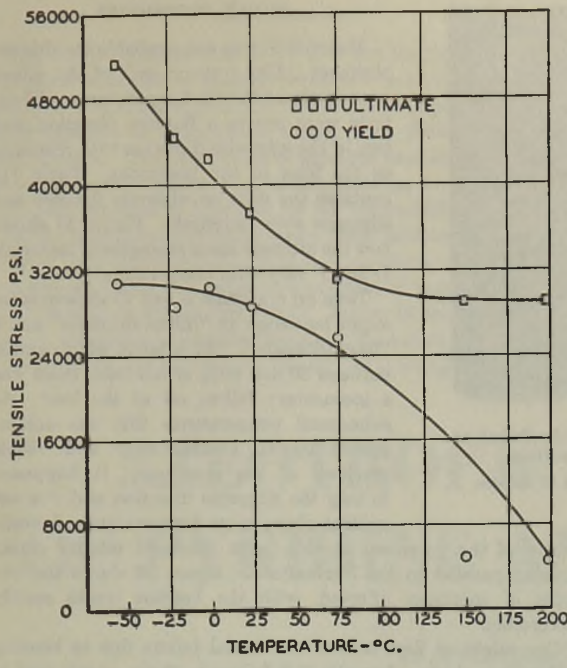

Figure 8. Temperature Effect on the Strength of Type F Laminate

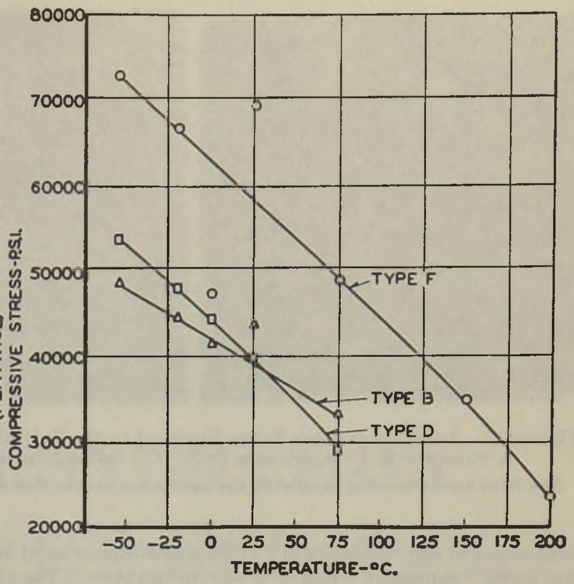

Figure 9. Effect of Temperature on Flatwise Compressive Strength of Laminate

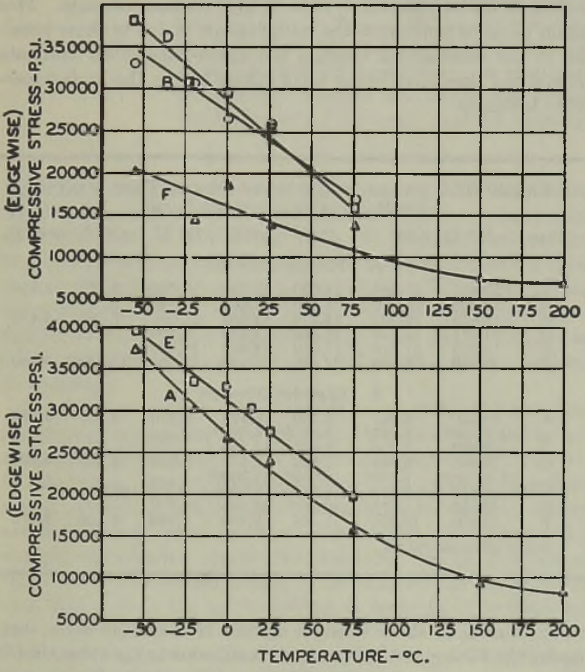

Figure 10. Effect of Temperature on Edgewise Compressive Strength of Laminates

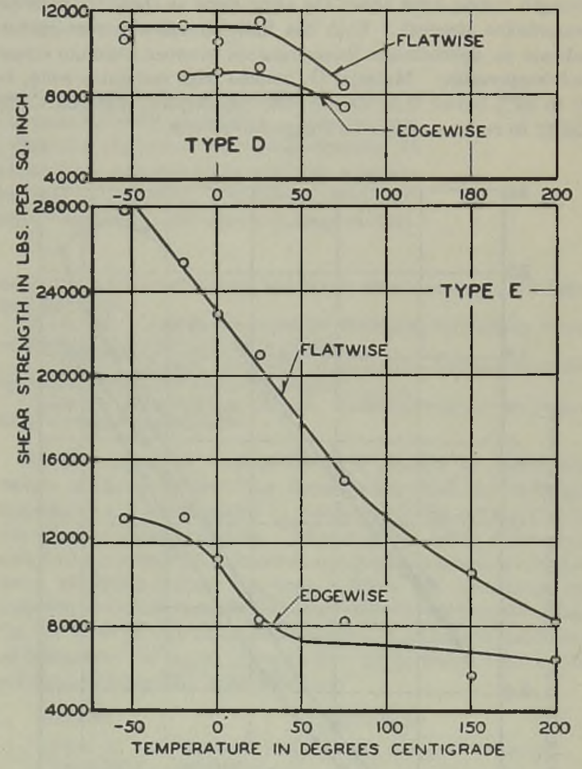

Figure 11. Effect of Temperature on Strength of Type D and Type E Laminates

G, which show a slower rate of decrease in strength with increase in temperature. Material F which contains Fiberglas filler gives about the same rate of decrease in strength as do the cellulose-filled materials. The significance of this fact appears to be that the resin is more critical than the filler in the range of temperatures employed in this test. The Fiberglas-filled laminate is 40% better in ultimate strength than any of the others (Figure 9).

The data for ultimate compressive strength in the edgewise direction is recorded in Table II*B* and was obtained according to the outlined procedure. Figure 10 shows graphically the effect of temperature on the edgewise compressive strength of plastics

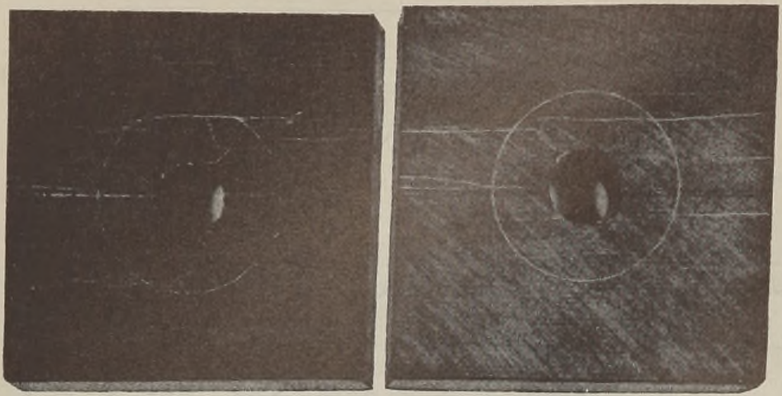

**Figure 12. Laminates after Being Stressed to the Initial Ultimate Point at a Subnormal Temperature (−20° C.) in an Edgewise Direction**

**The faint cracks running parallel to the lamination are the first indication of failure.**

laminates. In this case material F (Fiberglas-filled laminate) has the lowest compressive strength at any temperature. The significance is that the bond strength of Fiberglas-filled laminates is low and is reflected in the low value of its edgewise compressive strength.

In every case except for material F the edgewise compressive strength curves have about the same slope as those for flatwise compressive strength. Both the flatwise and edgewise curves indicate an approximate linear relation between ultimate stress and temperature. Material G, bonded with melamine resin, is 10 to 20% better than its phenolic counterpart, material C, in ability to resist an edgewise compressive force.

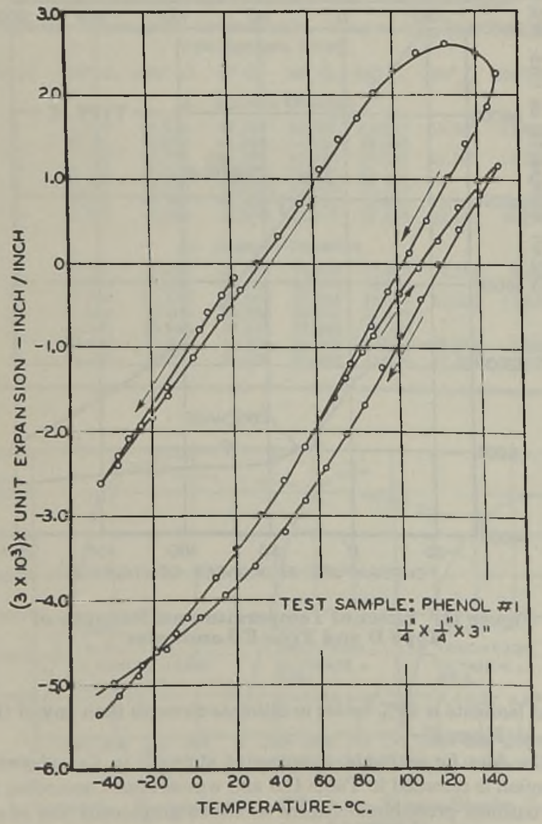

**Figure 13. Thermal Expansion Test on Micarta**

### SHEAR PROPERTIES

Material G was not available for this experiment. Five tests on each of the others were made at the six temperatures. Three tests were run in a flatwise direction and two in the edgewise direction with reference to the filler in the laminates. Table III contains the data on ultimate flatwise and edgewise shear strength. Figure 11 shows how the ultimate shear strengths of materials D and F vary with temperature.

Tests on materials B and D showed what might be called an "initial ultimate" and a "final ultimate". At a point which varied between 50 and 90% of full load, there was a momentary falling off of the load. At subnormal temperatures this was accompanied by an audible snap and visible cracking of the specimen; it happened in only the edgewise direction and was not evident above room temperature. Investigation of the specimen at this point disclosed minute cracks running parallel to the laminations. Figure 12 shows the two types of specimen affected, with the hairline cracks readily discernible.

One might at first believe this initial failure due to bending rather than shear. Actually it is failure in shear, except that in this case it is parallel to the laminations whereas the final failure occurs across the laminations. Material B, which contains a kraft paper filler, suffers the initial ultimate at 50 to 60% of its final ultimate; material D, which contains an alpha paper filler, suffers its initial ultimate at 70 to 90% of its final ultimate. This again tends to prove that the initial failure is due to shear parallel to the laminations because the alpha-paper-filled laminate should and does have better bond strength than the kraft-paper-filled laminate.

Table III. Average Ultimate Shear Test Values (in Pounds per Square Inch)

| Type | −56° C. | −20° C. | 0° C. | 25° C. | 75° C. | 150° C. | 200° C. |
|---|---|---|---|---|---|---|---|
| | | | *A.* Flatwise Direction | | | | |
| A | 20,660 | 17,420 | 16,630 | 15,320 | 10,080 | 5,770 | 2,150 |
| B | 18,030 | 12,060 | 13,010 | 13,460 | 9,340 | .... | .... |
| C | 18,850 | 16,300 | 15,200 | 14,650 | 11,060 | 7,580 | 4,480 |
| D | 11,275 | 11,320 | 10,530 | 11,480 | 8,400 | .... | .... |
| E | 19,570 | 17,270 | 17,410 | 14,800 | 10,025 | .... | .... |
| F | 27,900 | 25,420 | 22,850 | 20,970 | 15,000 | 10,550 | 8,350 |
| | | | *B.* Edgewise Direction | | | | |
| A | 10,250 | 8,065 | 8,250 | 8,175 | 6,070 | 3,950 | 3,330 |
| B | 7,000$^a$ | 4,540$^a$ | 3,965$^a$ | 6,650$^a$ | 6,960 | .... | .... |
| | 12,650 | 8,290 | 8,275 | 10,450 | | | |
| C | 11,065 | 8,945 | 7,550 | 8,425 | 7,425 | 5,825 | 4,000 |
| D | 9,250$^a$ | 7,500$^a$ | 6,650$^a$ | 7,300$^a$ | 7,460 | .... | .... |
| | 10,650 | 8,975 | 9,070 | 9,300 | | | |
| E | 13,275 | 11,075 | 10,565 | 13,625 | 10,200 | .... | .... |
| F | 13,200 | 13,200 | 11,265 | 9,870 | 8,240 | 6,130 | 6,575 |

$^a$ Initial ultimate values.

The curves of shear strength against temperature show that, again, the Fiberglas-filled laminate is superior to the others in the flatwise sense, but that the difference between its flatwise and edgewise shear strength is much greater than for the other materials. The loss in strength (for most of the materials tested) changes abruptly at room temperature. In several cases the rate of loss in strength is greater above room temperature; in a few cases it is less. This is similar to the phenomenon observed in the tensile tests and to a certain extent in the compressive tests.

The laminates which have a slower rate of strength loss above room temperature are of the mineral filled type—Fiberglas fabric and asbestos fabric

## CONCLUSIONS

The results of these tests show that the tensile, compressive, and shear strengths of phenolic laminates are inversely proportional to temperature, and that the cellulose-filled materials are more sensitive to temperature change than their mineral-filled counterparts. The rate of loss of strength as a function of temperature increases above room temperature for the cellulose-filled laminates, whereas it decreases for the mineral-filled materials.

At the time these test results were being analyzed, thermal expansion tests on paper-filled laminates were being conducted. It was noticed that a change in the coefficient of thermal expansion took place at approximately 60° C. Figure 13 shows the expansion *vs.* temperature characteristics of this material; the transition point can be located accurately by a straight edge. The temperature at which this transition occurs lies within the range where critical variation in the physical properties of the laminates was noted.

Many more determinations will have to be made before any general conclusion can be drawn with regard to the effect of second-order transition point on physical properties of laminates and of plastics in general. This phenomenon should be of general interest and must be considered in any future investigation of the effect of temperature on the physical properties of plastics and plastics laminates.

## ACKNOWLEDGMENT

The authors are pleased to acknowledge the assistance and suggestions of R. W. Auxier and P. G. McVetty of the Westinghouse Research Laboratories.

# AZEOTROPIC DEHYDRATION OF PYRIDINE AND ITS HOMOLOGS

LLOYD BERG, J. M. HARRISON,
AND C. W. MONTGOMERY
*Gulf Research & Development Company, Pittsburgh, Pa.*

**By means of the hydrogen bond classification of liquids, the search for entrainers for effecting a desired azeotropic separation is considerably simplified. This system is applied to the selection of entrainers suitable for the azeotropic dehydration of pyridine and its homologs. A number of satisfactory entrainers are listed, and experimental results are given for the dehydration of pyridine, 2-picoline, and 2,6-lutidine, using toluene, methyl isobutyl ketone, and propyl isobutyrate, respectively.**

IN THE study of azeotropic distillation, very little information has been presented to enable an investigator to select a suitable entrainer for a desired separation. Recently (*3*) a system was proposed for grouping all liquids into five classes, depending upon their hydrogen-bond-forming potentialities. The object of this paper is to make use of the generalizations derived from this classification in the selection of azeotropic systems, and specifically to determine suitable processes for the dehydration of pyridine and its homologs.

The high water-solubility of pyridine and its homologs makes its recovery from water-insoluble media easy to accomplish by extraction. The attractiveness of this method is lessened, however, by the difficulty of separating pyridine or its homologs from water. Pyridine, picolines, and lutidines form minimum-boiling azeotropes with water so that they cannot be separated by straight rectification alone. Furthermore, the composition of these azeotropes is high enough in the heterocyclic compound so that they contain too much pyridine or homolog to be discarded but an insufficient amount to be treated as reasonably pure. Previously reported work on the azeotropic dehydration of these heterocyclic compounds is limited (*2*, *5*).

## HYDROGEN BOND CLASSIFICATION OF LIQUIDS

Based on the hydrogen bond classification of liquids, generalizations concerning the probable nature of the azeotropes formed between any two classes of liquids can be made. Briefly the classes are as follows (*3*):

CLASS I. Liquids capable of forming three-dimensional networks of strong hydrogen bonds.

CLASS II. Other liquids composed of molecules containing both active hydrogen atoms and donor atoms (oxygen, nitrogen, and fluorine).

CLASS III. Liquids composed of molecules containing donor atoms but no active hydrogen atoms.

CLASS IV. Liquids composed of molecules containing active hydrogen atoms but no donor atoms.

CLASS V. All other liquids—i.e., liquids having no hydrogen-bond-forming capabilities.

By this system of classification it is possible to predict the nature of the deviations from Raoult's law, and the hydrogen bonding in a mixture makes it possible to judge approximately the extent of these deviations. When a system which shows positive (+) deviations from Raoult's law forms an azeotrope, it will be a minimum-boiling azeotrope. When the deviations are negative (−), any azeotrope formed will be maximum boiling. On the basis of this liquid classification, a systematic summary of deviations for water (class I) and the pyridine heterocyclic compounds (class III) is the following:

| CLASSES | DEVIATIONS |
|---|---|
| I and V | Always (+) deviations; frequently limited solubility |
| I and IV | |
| I and I | Usually (+) deviations; very complicated groups |
| I and II | |
| I and III | |
| III and II | |
| III and IV | Always (−) deviations |
| III and III | Quasi-ideal systems; always (+) deviations or ideal |
| III and V | |

## ENTRAINER PROPERTIES

With the understanding of azeotrope formation afforded by this classification, it is possible to design methods for separating

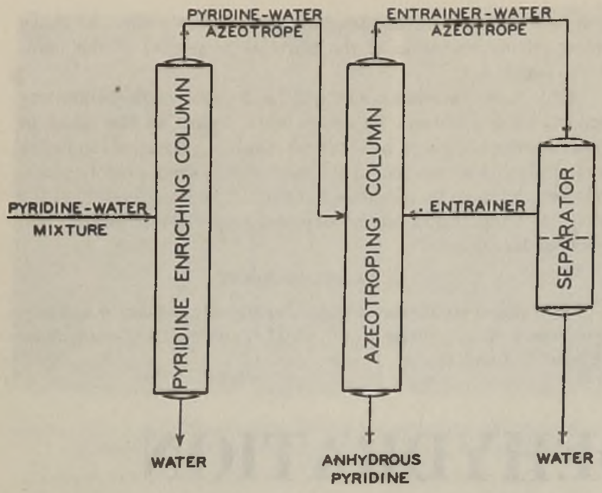

**Figure 1. Flow Sheet for the Azeotropic Dehydration of Pyridine**

water from pyridine or its homologs. The ideal entrainer to effect such separations should have the following properties:

1. Form a minimum azeotrope with water at a temperature below the temperature of the water-heterocyclic compound minimum azeotrope—for example, below 92° C. for pyridine, below 95° C. for 2-picoline, and below 96° C. for 2,6-lutidine.
2. Form no minimum azeotrope with pyridine or its homologs. Theoretically, it would be necessary only that the minimum azeotrope boil above the entrainer-water azeotrope. Actually, however, when each possible pair in a three-liquid system forms a minimum azeotrope, a ternary azeotrope is always formed.
3. Form no ternary azeotrope with water and the heterocyclic compound.
4. Remove a large amount of water per part of entrainer.
5. Be insoluble in water at room temperature. This will allow a phase separation so that the entrainer may be readily recovered.

As the list of deviations above shows, because of their high water solubility and their tendency toward azeotrope formation with the pyridine heterocyclic compounds, class I and class II liquids may be eliminated from consideration. Entrainers suitable to effect this separation will be found among class III, IV, and V liquids. Pyridine and its homologs are class III liquids and form quasi-ideal solutions with other liquids of class III. Minimum-boiling azeotropes will form only when the boiling points of the two class III liquids are close together. Pyridine or its homologs will form no minimum azeotropes with class IV liquids. Any azeotropes formed will be maximum and will not affect the operation of this process. All class IV liquids forming azeotropes with water boiling below the temperature of the heterocyclic compound–water azeotrope can be used. Class V liquids form quasi-ideal solutions with pyridine or its homologs and do not form azeotropes unless they boil very close to the heterocyclic compound.

Some suitable entrainers for dehydration of pyridine, 2-picoline, and 2,6-lutidine are listed in Table I. For use in a batch operation, almost any entrainer having the properties outlined above will be satisfactory. Whether the pyridine-water azeotrope is merely suppressed from the distillate, or whether it is destroyed by the creation of the more volatile entrainer-water azeotrope, no difficulty is encountered in obtaining a pyridine-free overhead. Even if a stable pyridine-water azeotrope does exist in the column, the separation is readily effected although the boiling point difference between the two azeotropes may be small. The ease of separation appears to be largely determined by the relationship of the activity coefficients (*1*).

In continuous operation the composition of the feed is more critical. If an excess of entrainer is used, then it too must be separated from the pyridine. If the entrainer is more volatile than pyridine, then the stripping section of the column must be sufficient to separate them. If the entrainer is less volatile than pyridine, then the excess entrainer appears in the residue, and this pyridine-entrainer mixture has to be re-rectified to obtain pure pyridine. Thus, the equilibrium relation for the entrainer-pyridine system is an important factor.

## OPERATION OF PROCESS

Figure 1 is a flow diagram for the dehydration of pyridine. The pyridine-water mixture passes through a heat exchanger and is fed to the enriching column where the pyridine-water azeotrope is removed as overhead and excess water is taken off as bottoms. This step is not essential to the process but greatly reduces the quantity of entrainer which is handled in subsequent steps. After being preheated, the pyridine-water azeotrope is charged to the azeotroping column where it is admixed with a sufficient quantity of entrainer. Anhydrous pyridine is recovered as bottoms product while the entrainer-water azeotrope is taken off overhead. This distillate goes to the separator where phase separation allows removal of water from the system and the recycling of the entrainer to the azeotroping column. The following examples show the dehydration of pyridine, 2-picoline, and 2,6-lutidine using as entrainers toluene, methyl isobutyl ketone, and propyl isobutyrate, respectively.

EXAMPLE 1. A batch rectification was made in a column of approximately twenty theoretical plates, packed with 1/4-inch stainless steel carding teeth and run at a reflux ratio of about 8 to 1. The charge consisted of 76 parts of pyridine, 64 parts of water, and 293 parts of toluene. This pyridine-water ratio represented the azeotropic composition obtained as distillate from the enrich-

TABLE I. ENTRAINERS FOR DEHYDRATION OF PYRIDINE, 2-PICOLINE, AND 2,6-LUTIDINE

| Class | Entrainer | B. P. at 760 Mm., ° C. | Water Azeotrope Temp., ° C. (*6*) | Parts Entrainer to Remove 1 Pt. Water (*6*) | Water Solubility, Pt./100 Pt. Water (*4*) |
|---|---|---|---|---|---|
| | **Entrainers for Pyridine** | | | | |
| III | Isobutyl formate | 98.2 | 80.4 | 11.8 | 1.0 |
| | Ethyl propionate | 99 | 81.2 | 9.0 | 2.4 |
| | Methyl butyrate | 102 | 82.7 | 7.7 | 1.5 |
| | Ethyl isobutyrate | 111.7 | 85.2 | 5.6 | Sl. sol.[a] |
| | Di-isobutyl ether | 122.2 | 88.6 | 3.4 | Sl. sol. |
| | Amyl formate | 132 | 91.6 | 2.5 | Sl. sol. |
| IV | Ethylene chloride | 83 | 72 | 11 | 0.9 |
| | 1,2-Dichloropropane | 96.8 | 78 | 7.4 | 0.3 |
| V | Benzene | 80.2 | 69.3 | 10.2 | 0.1 |
| | Toluene | 110.7 | 84.1 | 6.4 | Insol. |
| | **Entrainers for 2-Picoline** | | | | |
| III | Ethyl propionate | 99 | 81.2 | 9.0 | 2.4 |
| | Methyl butyrate | 102 | 82.7 | 7.7 | 1.5 |
| | Ethyl isobutyrate | 111.7 | 85.2 | 5.6 | Sl. sol. |
| | Methyl isobutyl ketone | 115.9 | 87.9 | 3.3 | 1.9 |
| | Isobutyl propionate | 136.9 | 92.8 | 2.1 | V. sl. sol.[b] |
| | Propyl butyrate | 142.8 | 94.1 | 1.7 | 0.2 |
| IV | 1,2-Dichloropropane | 96.8 | 78 | 7.4 | 0.3 |
| | 1,1,2-Trichloroethane | 113.5 | 86.1 | 6.0 | Insol. |
| V | Benzene | 80.2 | 69.3 | 10.2 | 0.1 |
| | Toluene | 110.7 | 84.1 | 6.4 | Insol. |
| | **Entrainers for 2,6-Lutidine** | | | | |
| III | Ethyl propionate | 99 | 81.2 | 9.0 | 2.4 |
| | Methyl butyrate | 102 | 82.7 | 7.7 | 1.5 |
| | Butyl formate | 106.8 | 84 | 5.5 | Sl. sol. |
| | Propyl propionate | 123.4 | 88.9 | 3.4 | 0.5 |
| | Propyl isobutyrate | 134 | 92.2 | 2.2 | V. sl. sol. |
| | Methyl phenyl ether | 154 | 95.5 | 1.5 | Insol. |
| IV | 1,2-Dichloropropane | 96.8 | 78 | 7.4 | 0.3 |
| | 1,1,2-Trichloroethane | 113.5 | 86.1 | 6.0 | Insol. |
| V | Benzene | 80.2 | 69.3 | 10.2 | 0.1 |
| | Toluene | 110.7 | 84.1 | 6.4 | Insol. |

[a] Slightly soluble. [b] Very slightly soluble.

ing column. The overhead from the above charge was a constant-boiling mixture (boiling point, approximately 85° C.) containing all of the water and toluene, while the anhydrous pyridine remained as bottoms product. The water was decanted from the toluene; this completely separated the three components of the original charge. If, instead of the azeotropic composition, a water-rich mixture containing 67% water and 33% pyridine were charged to the azeotrope column, then 704 parts of toluene would be required to dehydrate the same quantity of pyridine as before. Thus the value of the enriching column is evident. The distillation of the pyridine-water azeotrope and toluene is shown in Figure 2.

Example 2. A batch rectification was made of a charge consisting of 114 parts of 2-picoline, 86 parts of water, and 300 parts of methyl isobutyl ketone. The overhead was the water-ketone azeotrope, boiling at about 88° C.; the bottoms product was anhydrous 2-picoline. Phase separation of the distillate gave water and substantially pure ketone. This distillation is illustrated in Figure 3.

Example 3. A batch rectification was made of a charge consisting of 104 parts of 2,6-lutidine, 75 parts of water, and 187 parts of propyl isobutyrate. The overhead was the water-ester azeotrope, boiling at about 92.5° C.; the bottoms product was anhydrous 2,6-lutidine. Phase separation of the distillate gave water and essentially pure ester. This distillation is illustrated in Figure 4.

While 2-picoline and the lutidines are immiscible with hot water, complete dehydration cannot be obtained by phase separation because, even when hot, considerable water is still dissolved in the heterocyclic compound.

ACKNOWLEDGMENT

The authors are grateful for the suggestions of V. N. Hurd who reviewed the manuscript.

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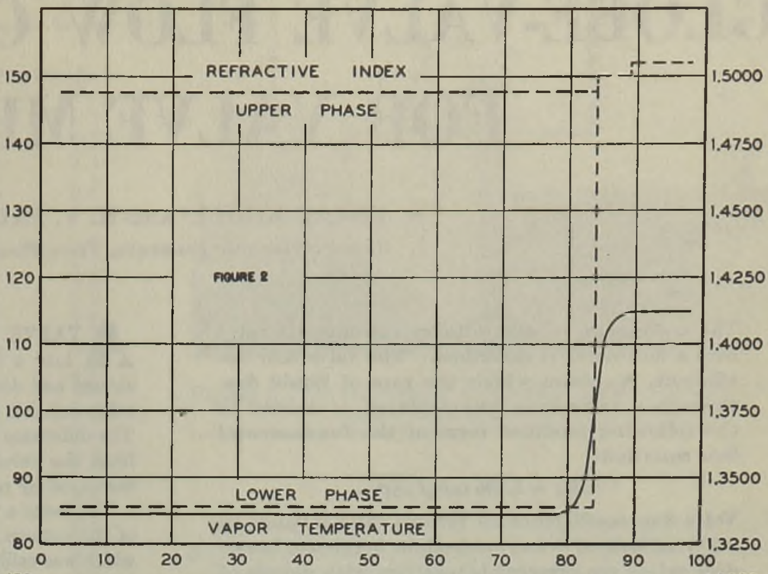

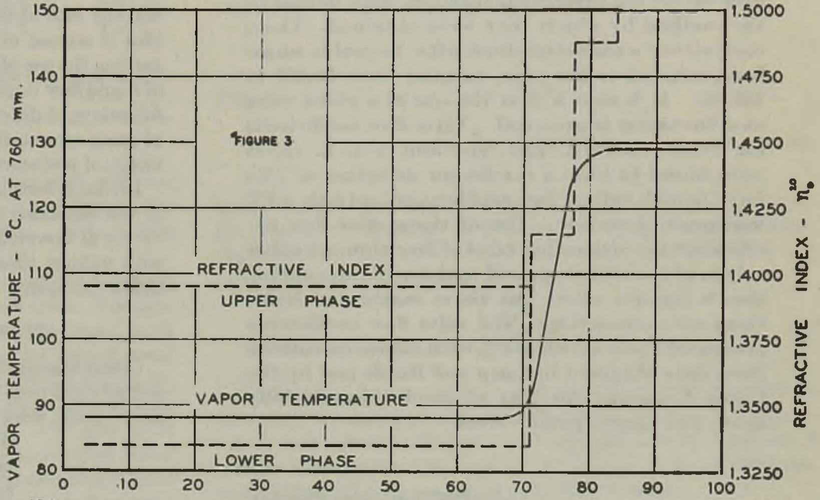

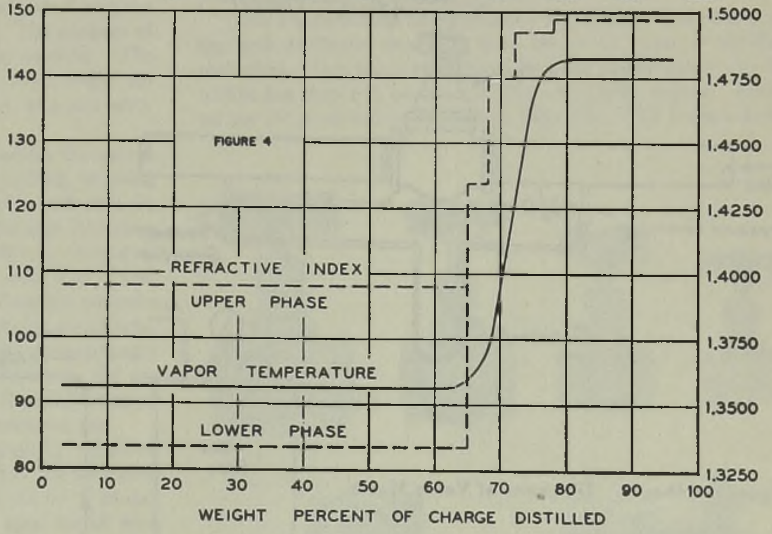

**Figure 2.** Distillation Curve for Dehydration of Pyridine Using Toluene

**Figure 3.** Distillation Curve for Dehydration of 2-Picoline Using Methyl Isobutyl Ketone

**Figure 4.** Distillation Curve for Dehydration of 2,6-Lutidine Using Propyl Isobutyrate

# GLOBE-VALVE FLOW COEFFICIENTS FOR VALVE METERS

A. EDGAR KROLL[1] AND H. V. FAIRBANKS
*Rose Polytechnic Institute, Terre Haute, Ind.*

**The conversion of an ordinary commercial valve into a flowmeter is described. The valve flow coefficient, $K_v$, from which the rate of liquid flow through a valve may be calculated, is defined in the following modified form of the fundamental flow equation:**

$$K_v = 1.496\, w/\sqrt{\rho \Delta P_i}$$

**Valve flow coefficients for various valve settings on different sizes of Crane brass-globe bevel-seat brass-disk valves are presented, together with details of the method by which they were obtained. These coefficients were determined with Reynolds numbers, referred to the pipe, ranging from 30,000 to 150,000. It is shown that the use of a globe valve as a flowmeter is practical. Valve flow coefficients for three different $^1/_2$-, $^3/_4$-, and 1-inch valves were found to have a maximum deviation of 5%; for $1^1/_4$-inch valves, flow coefficients had only a 3% maximum deviation. Use of these valve flow coefficients for computing rates of flow through other valves, of the same type and make, without calibration is feasible where the above maximum deviations are permissible. The valve flow coefficients presented agree within 3.0% with values calculated from data obtained by Corp and Ruble and by the Crane Company for loss of head through fully open, new Crane globe valves.**

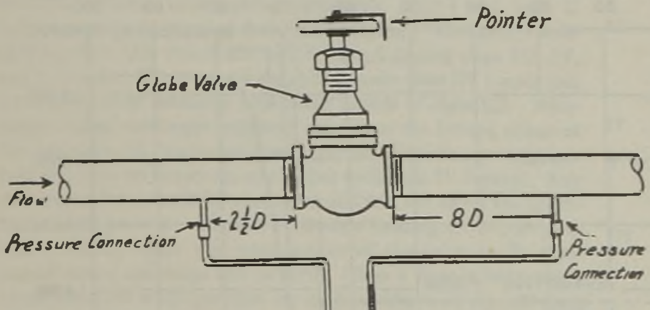

Figure 1 (*Above*). Diagram of Valve Meter

A VALVE meter is an ordinary commercial valve converted into a flowmeter by attaching pressure connections upstream and downstream from the valve to a manometer or any other suitable pressure measuring device, as shown in Figure 1. The difference between the pressures upstream and downstream from the valve, caused by the smaller valve opening, can be measured by means of the manometer.

The use of a valve as a flowmeter was recently suggested by one of the authors. Data were given on a single 2-inch globe valve which was calibrated and used successfully to determine and control the rate of flow in a pipe line (*6*). In continuation of this idea it seemed of interest (*a*) to obtain further information regarding the use of valves for determining and controlling the rate of liquid flow in pipe lines, (*b*) to determine valve flow coefficients for valves of different sizes, and (*c*) to investigate the feasibility of using commercial valves as flowmeters without calibration by virtue of predetermined flow coefficients.

Investigations in this field appear to be lacking, since a search of the literature revealed no information relative to the use of valves as flowmeters. This paper describes the results obtained with various sizes of brass globe valves manufactured by the Crane Company.

### APPARATUS AND METHOD OF TESTING

Crane brass-globe valves, No. 1, with bevel seat, brass disk, and screwed ends were used; sizes were $^1/_2$ to $1^1/_4$ inches, inclusive. Runs were made on three different valves of each size. All the valves were new except one $1^1/_4$-inch and one 1-inch valve, which were used but in good condition. The results obtained on the used valves were in good agreement with those on the new valves. Water temperature was 60° F. in all cases, with the flow upward through the valve orifice.

Figure 2 is a diagram and Figure 3 is a photograph of the apparatus. In all tests the valve was preceded by fifteen pipe diam-

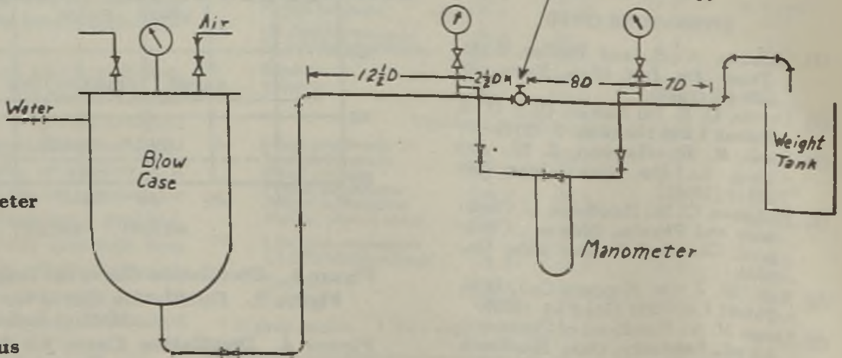

Figure 2 (*Right*). Diagram of Apparatus

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[1] Present address, E. I. du Pont de Nemours & Company, Inc., Childersburg, Ala.

Table I. Summary of Calculated Results on Globe Valves

| No. of Turns Open | Valve Size$^a$, Inches | Mean Value of $K_v$ | Deviation, % Av. | Deviation, % Max. |
|---|---|---|---|---|
| 1/4 | 1/2 | 0.021 | 4.4 | 6.3 |
| 1/2 | | 0.043 | 2.1 | 3.1 |
| 1 | | 0.074 | 1.0 | 1.4 |
| 1 1/2 | | 0.090 | 3.3 | 4.5 |
| 2 | | 0.095 | 1.0 | 1.4 |
| 3 | | 0.100 | 0.4 | 0.7 |
| 4 3/8$^b$ | | 0.100 | 0.7 | 1.0 |
| 1/4 | 3/4 | 0.036 | 3.1 | 4.8 |
| 1/2 | | 0.071 | 1.8 | 2.8 |
| 1 | | 0.126 | 1.0 | 1.6 |
| 1 1/2 | | 0.152 | 1.3 | 2.0 |
| 2 | | 0.173 | 0.9 | 1.3 |
| 3 | | 0.196 | 0.9 | 1.4 |
| 4 | | 0.201 | 1.2 | 1.8 |
| 4 3/8$^b$ | | 0.209 | 1.5 | 2.3 |
| 1/4 | 1 | 0.052 | 4.9 | 6.1 |
| 1/2 | | 0.108 | 1.7 | 2.5 |
| 1 | | 0.207 | 0.9 | 1.3 |
| 1 1/2 | | 0.248 | 3.0 | 4.8 |
| 2 | | 0.283 | 2.5 | 5.0 |
| 3 | | 0.326 | 3.5 | 4.9 |
| 4$^b$ | | 0.341 | 2.3 | 3.4 |
| 1/4 | 1 1/4 | 0.072 | 2.2 | 3.2 |
| 1/2 | | 0.150 | 1.6 | 2.5 |
| 1 | | 0.278 | 1.2 | 1.8 |
| 1 1/2 | | 0.361 | 2.0 | 3.1 |
| 2 | | 0.423 | 1.8 | 2.8 |
| 3 | | 0.470 | 1.9 | 2.9 |
| 4 | | 0.507 | 1.2 | 1.8 |
| 4 5/8$^b$ | | 0.520 | 1.9 | 2.9 |

[a] Three valves were used for each setting.
[b] Approximate. Different valves varied slightly in the number of turns to fully open.

eters of straight galvanized steel pipe and was followed by fifteen pipe diameters of similar pipe and a gooseneck (*1*) in which the rise was always greater than six pipe diameters. Some of the valves used are pictured in Figure 4.

The rate of water discharge was measured at various pressures and valve settings, taken as the number of turns open. For convenience in setting the number of turns open, only round valve handles were used and were equipped with a narrow strip of metal bent at a right angle, pointed on one end and having a hole in the other so that it could be fastened on the valve stem together with the valve handle as shown in Figures 1 and 3. The zero point was determined by first opening the valve wide, allowing water to flow for a few seconds, and then closing the valve slowly until the flow just stopped. The metal pointer was attached and the number of turns open were set from this point. The purpose of this method of determining the zero point was twofold: The valve was flushed clean of any foreign material which might obstruct the flow until the valve was fully opened, and any error due to slack in the valve stem was eliminated.

The taps for determining the pressure drop across the valves were made by first welding on a 1/4-inch half-coupling, screwing in a short nipple, and then drilling holes with a 1/4-inch drill (*5*) two and a half pipe diameters upstream and eight pipe diameters downstream from the valve. Great care was taken to remove all burrs from the edges of the holes on the inside wall of the pipe. These openings were connected to calibrated Bourdon pressure gages for large differential pressures and to a mercury manometer for small differential pressures. Readings on the pressure gages were taken to the nearest 0.5 pound per square inch on the upstream gage and to the nearest 0.2 pound on the downstream gage. The manometer readings were taken to the nearest 0.1 cm.

The quantity of water discharged was determined by weight on Fairbanks platform scales of 1000-pound capacity. In determining the rate of discharge, the time was measured by a Kodak timer. The Reynolds number, referred to the pipe, for all runs varied from 30,000 to 150,000. The source of water supply for the investigation was a blow case which furnished the various pressures, ranging from 10 to 40 pounds per square inch. During any one run, constant pressure was maintained.

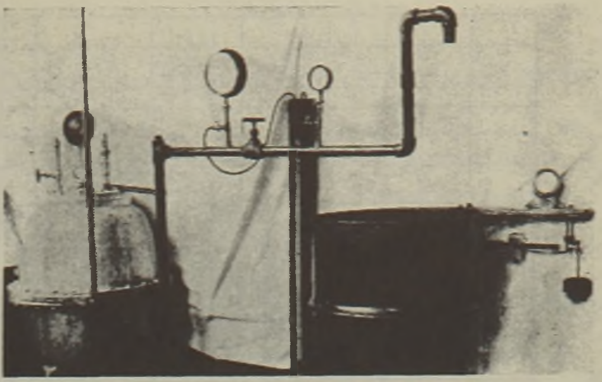

Figure 3. Photograph of Apparatus Used in Determining Globe-Valve Flow Coefficients

DISCUSSION AND RESULTS

The working equation for computing the actual rate of liquid flow through an orifice, adopted by the A.S.M.E. Special Research committee on fluid meters (*2*, *7*), is

$$w = KA_2\sqrt{2g\rho(p_1 - p_2)} \tag{1}$$

For this study Equation 1 was modified to

$$w = \frac{K_v}{12}\sqrt{2g\rho\,\Delta P_i} \tag{2}$$

where $K_v$, the valve flow coefficient, as defined here, differs from the standard orifice flow coefficient (*2*) only in that it includes the cross-sectional area of the discharge opening and is not dimensionless. Simplifying Equation 2,

$$K_v = \frac{1.496\,w}{\sqrt{\rho\,\Delta P_i}} \tag{3}$$

Globe-valve flow coefficients calculated from data obtained in this study are shown graphically on logarithmic paper in Figure 5. These valve flow coefficients were calculated from Equation 3 using values obtained by measuring the rate of water discharge and differential pressure at various valve settings.

Table I summarizes the calculated results and shows the average and maximum deviation from the mean value of the flow coefficient. One valve reproduces the results of another, usually within less than 5% on the 1/2-, 3/4-, and 1-inch valves; results on the 1 1/4-inch valves varied less than 3%. The largest devia-

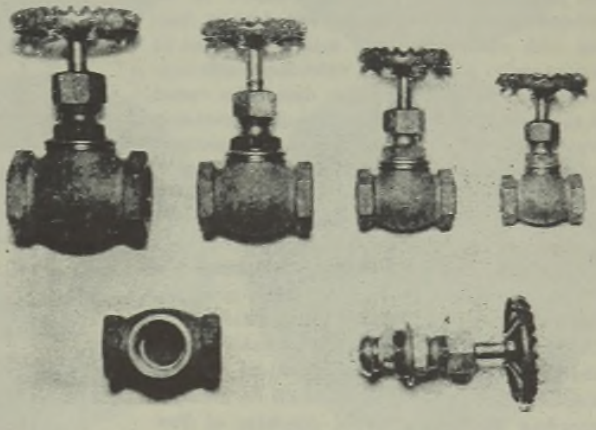

Figure 4. Photograph of Globe Valves

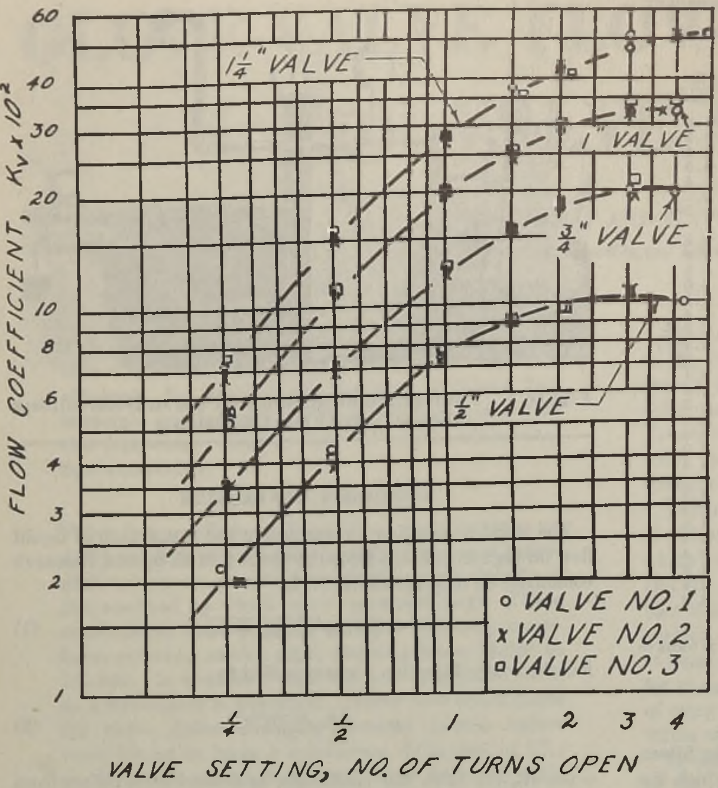

**Figure 5. Globe-Valve Flow Coefficients at Various Valve Settings**

tions were obtained at 1/4 turn open, which were probably due to variations in the valve settings or flow characteristics at close throttling conditions. The valve settings are less critical as the opening increases. There is also danger of wiredrawing the seat when the flow is throttled down to 1/4 turn open. For these reasons use of the 1/4 turn open setting is not recommended.

Even with the favorable agreement shown above, it should be pointed out that valve flow characteristics are influenced considerably by manufacturing variations, design details such as type of disk, contour of body, etc., and direction of flow through the valve orifice, so that use of the flow coefficients given here should be restricted to the type and make tested, since their use with other types and makes may lead to serious error. For example, valve flow coefficients determined for a composition disk valve varied as much as 30% from the brass-disk bevel-seat type. It is felt, however, that with consistent design and manufacture the average flow coefficients for the commonly used globe valves could be determined; this would make possible their use as flowmeters without calibration, provided the deviation and accuracy are stipulated.

The valve flow coefficient curves given in Figure 5 may be used for computing rates of flow through these Crane valves without calibration, where the above maximum deviations are permissible. The pressure taps should be installed according to Figure 1, the direction of flow is upward through the orifice, and the weight rate of flow, $w$, is calculated from Equation 3. While it is known that there is little variation in orifice flow coefficients with Reynolds numbers above 30,000 (7), it should be noted that the valve flow coefficients presented here were determined with Reynolds numbers, referred to the pipe, between 30,000 and 150,000.

Figure 6 shows the flow characteristics of the globe valves used. The values for percentage of total flow and percentage of total turns open were calculated from the mean values of the flow coefficients given in Table I, assuming a constant pressure drop. Table II compares valve flow coefficients obtained in this study with those calculated from data obtained by Corp and Ruble (3) and the Crane Company (4) for loss of head through fully open Crane globe valves. The present data compare favorably for the 3/4- and 1-inch valves tested by Corp and Ruble in 1919, being 0.5% higher and 2.9% lower, respectively. The 1/2-inch valve is 20,5% higher. This unfavorable agreement may be due to the fact that the 1/2-inch valves were tested by Corp and Ruble with Reynolds numbers less than 20,000. The Crane Company's value for the 1/2-inch valve flow coefficient was calculated from $k = 10.0$ in the equation $H = kV^2/2g$ given in the reference for globe valves (4). Agreement within 3.1% is shown here.

### SUMMARY AND CONCLUSION

1. Valve flow coefficients have been given for various valve settings on Crane 1/2-, 3/4-, 1-, and 1 1/4-inch brass-globe valves No. 1 with bevel seat and brass disk. The flow coefficients were determined with Reynolds numbers, referred to the pipe, ranging from 30,000 to 150,000.

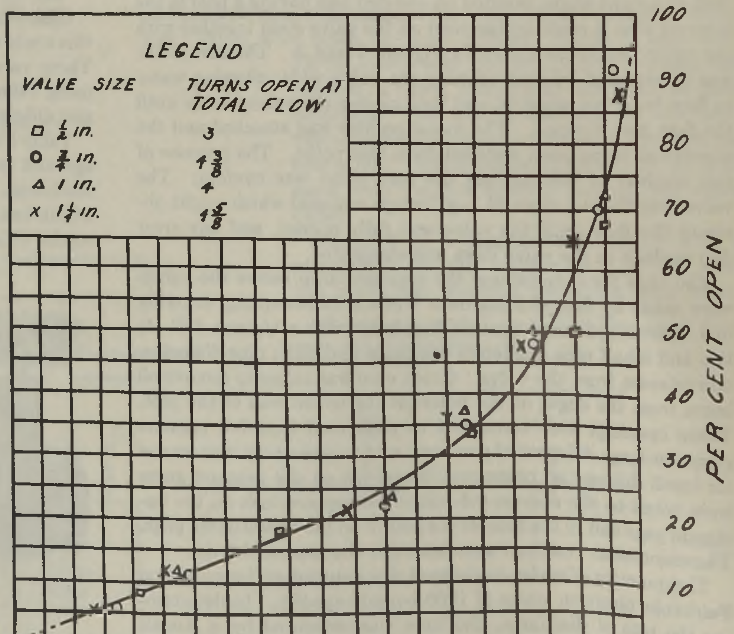

**Figure 6. Flow Characteristics of Globe Valves with Flow Upward through the Orifice and Based upon a Constant Pressure Drop**

Table II. Valve Flow Coefficients Calculated from Equation 3, Using Data Obtained by Corp and Ruble (*5*) and the Crane Company (*4*) for Loss of Head through Globe Valves as Compared to Coefficients Obtained in This Study

| | Fully Open $K_v$ for Valve Size of: | | |
|---|---|---|---|
| | 1/2 in. | 3/4 in. | 1 in. |
| Corp and Ruble (1922) | 0.083[a] | 0.208 | 0.351 |
| Crane Co. | 0.097[b] | .... | .... |
| Kroll and Fairbanks (1944) | 0.100 | 0.209 | 0.341[c] |

[a] Used valves at Reynolds numbers less than 20,000.
[b] Calculated from $k = 10.0$ in $H = kV^2/2g$.
[c] One used valve.

2. The ordinary commercial globe valves of the type and make used in this study may be used as flowmeters without calibration by use of the valve flow coefficient, $K_v$, from which the rate of flow may be calculated, where a maximum error of 5% is permissible.

3. Greater precision with larger size valves is indicated by the fact that the maximum deviation for the 1 1/4-inch valves was only 3%.

4. The principal advantages of a valve meter are: (*a*) It may be used as an adjustable orifice for widely varying conditions of flow; (*b*) the valve is already in the pipe line and hence there is no increased resistance to flow; (*c*) little initial cost is incurred by converting a valve into a flowmeter; and (*d*) the upkeep is small.

## ACKNOWLEDGMENT

Thanks are due to B. E. Hunt for the drawings and to F. M. Lundgren who took the pictures of the valves and apparatus used.

## NOMENCLATURE

$A_2$ = cross-sectional area of discharge opening, sq. ft.
$D$ = diameter of pipe, ft.
$g$ = acceleration due to gravity, 32.17 (ft./sec.)/sec.
$H$ = loss of head, feet of fluid
$k$ = coefficient, dimensionless
$K$ = flow coefficient, dimensionless
$K_v$ = $KA_2$ = valve flow coefficient, sq. ft.
$p_1, p_2$ = pressures at upstream and downstream pressure taps, respectively, lb./sq. ft.
$\Delta P_i = \frac{p_1 - p_2}{144}$ = differential pressure, lb./sq. in.
$V$ = velocity of water, ft./sec.
$w$ = weight rate of discharge, lb./sec.
$\rho$ = density, lb./cu. ft.

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(3) Corp and Ruble, Univ. Wisconsin Eng. Expt. Sta., *Bull.* 9, No. 1 (1922).
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(5) Gess, Louis, *Instrumentation*, 1, No. 2, 26 (1944).
(6) Kroll, A. E., *Chem. & Met. Eng.*, 51, No. 7, 114 (1944).
(7) Perry, J. H., Chemical Engineers Handbook, 2nd ed., p. 848, New York, McGraw-Hill Book Co., 1941.

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# Interchain Order and Orientation in Cellulose Esters—Correction

An unfortunate error occurred in connection with Figure 5 of this article by W. O. Baker in the March, 1945, issue of Industrial and Engineering Chemistry, page 252. Each x-ray diagram of this figure as printed in the original article should be considered as rotated by 90° so that the fiber axis, shown horizontally, becomes vertical.

Poor reproduction, due to the quality of paper now available, destroyed the diagrams; Table III (page 253) gives the actual features. Figure 5 is reproduced here, placed and captioned correctly.

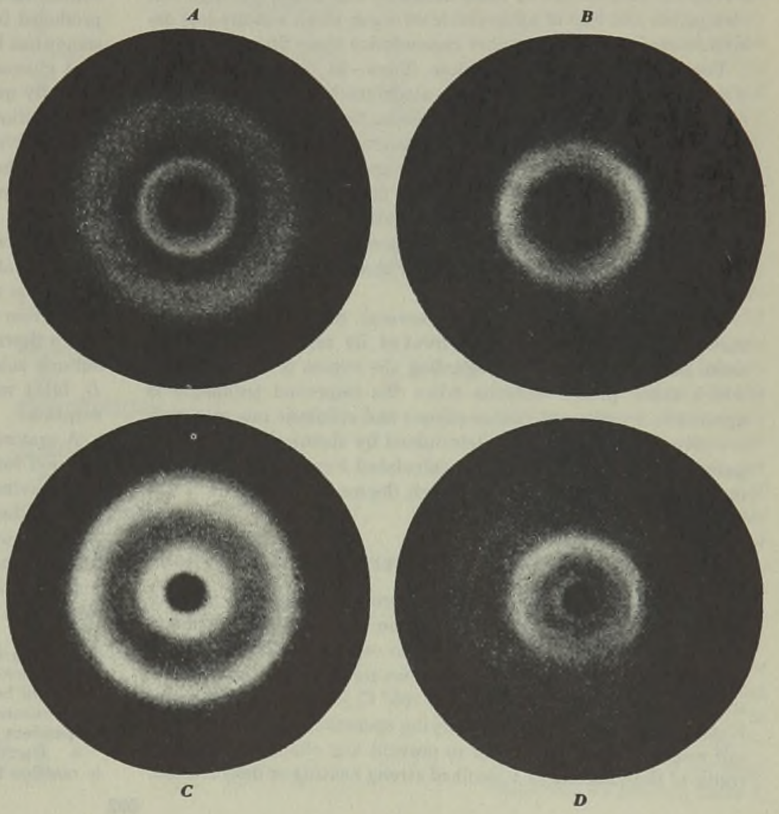

Figure 5. X-Ray Diagrams of Starch Triesters

*A.* Tapioca starch triacetate, unoriented
*B.* Cornstarch triacetate, drawn uniaxially
*C.* Tapioca starch tributyrate, unoriented
*D.* Potato starch tripropionate, oriented

# Chemical Characterization of Rayon Yarns and Cellulosic Raw Materials

C. C. CONRAD AND A. G. SCROGGIE
*Rayon Department, E. I. du Pont de Nemours & Company, Richmond, Va.*

**The hydrolysis and catalytic oxidation of cellulose (*4, 5, 6, 7, 9*) by hydrochloric acid in the presence of ferric chloride is applied to the characterization of a number of rayon yarns and cellulosic raw materials used in rayon manufacture. The amount of carbon dioxide evolved from the cellulosic materials is compared with the amount evolved from glucose to obtain an estimate of the most reactive material. This estimate is called the "accessibility" of the material. Accessibility is revealed as showing a high degree of correlation with certain x-ray parameters and substantiates to a certain degree the contention that accessibility is chiefly a measure of amorphous cellulose. Accessibility is also shown to vary inversely with the alpha cellulose content of native celluloses. Modifications of the characterization technique are described which lead to an improved reproducibility for the method. Additional data are given on the reaction between glucose and the system hydrochloric acid–ferric chloride.**

THE development of the rayon industry has resulted in the production of a series of fiber types having a wide variety of properties. Uniformity of properties is a characteristic which can be relied upon, because the fibers are manufactured, under close chemical and physical control, from a uniform supply of cellulose. Familiar properties characterizing these cellulosic fibers as currently produced are: controlled filament length, uniform strength and elongation, resistance to certain types of mechanical flexing, controlled luster, brilliant and uniform dyeing, and high dry strength. In contrast to these desirable attributes, the high wet elongation and loss of appreciable strength when wet are less desirable qualities which further characterize these fibers.

For such regenerated cellulose fibers—in fact for all fibers whether natural or man-made—attempts have been made to characterize their chemical and physical behavior by hypotheses concerning their internal molecular structure. Studies by Nickerson (*4, 5, 6, 7, 9*) on the hydrolysis and catalytic oxidation of cellulose by hydrochloric acid in the presence of ferric chloride show differences in the degree of reactivity of cellulose, depending on the history of the sample. Our interest in this field has been to apply this chemical method to the characterization of a number of cellulosic materials.

The work reported presents several modifications of the method which have greatly improved its reproducibility, and some information is given regarding the extent of the oxidation which takes place. Results when the improved technique is applied to a variety of viscose rayons and cellulosic raw materials are given. Accessibility as determined by chemical tests is compared with the "crystallinity", calculated from x-ray diffraction intensity measurements, and a high degree of correlation is observed in the rayons tested.

## PREPARATION OF SAMPLES AND EXPERIMENTAL METHOD

All tests on cellulosic materials were carried out on samples conditioned to an equilibrium moisture content at 60% relative humidity and 75° F. (24° C.). The oven-dry cellulose in the sample was calculated from the moisture regain of a duplicate sample dried to constant weight at 105° C. in a current of dry air. Elimination of an actual oven-drying operation on the sample itself was a safeguard provided to prevent any change in the reactivity of the material as a result of strong heating or dehydration.

The glucose used in this work was Merck reagent-grade anhydrous dextrose. It was dried to constant weight at 105° C. before use.

The apparatus is essentially that described by Nickerson (*7*) with the exception of certain modifications designed to improve the reproducibility of carbon dioxide evolution and assist in convenience of operation. This characterization test is based on the fact that carbon dioxide is evolved from glucose by hydrochloric acid–ferric chloride reagent at a rate proportional to the glucose concentration. Under similar conditions carbon dioxide is also produced from cotton and other cellulosic materials although at somewhat lower rates. The mechanism proposed for cellulose is that glucose is first produced by hydrolysis and is subsequently partially oxidized to carbon dioxide. Thus, the ratio of the rate of evolution of carbon dioxide for glucose to that for the test sample gives a measure of the amount of material hydrolyzed.

In conducting the hydrolysis, samples of glucose (1.4 to 1.6 grams) or cellulosic materials (1.2 to 1.6 grams) are digested with 150 ml. of reagent (2.4 ± 0.01 $N$ hydrochloric acid and 0.6 ± 0.01 $M$ ferric chloride) at its boiling point. The arrangement of the apparatus is shown in Figure 1. The essential features of the apparatus are: a purification train, *A*, for removing carbon dioxide from the carrier air stream (the train includes a manometer and a flowmeter); a reaction flask, *B*, with stirrer; condenser, sulfuric acid trap, and purification tubes, *C;* and Nesbitt bulbs, *D*, filled with Ascarite-Drierite mixture for carbon dioxide adsorption.

A gravimetric method for determining carbon dioxide is substituted for the volumetric method described by Nickerson (*7*). The gravimetric method appears to be superior to the volumetric, and this behavior is supported by independent observations (*8*). Actual practice has been to set up the equipment in duplicate, utilizing the same oil bath so that check runs on a sample can be made at the same time. The hydrolysis and catalytic oxidation are carried out under the following set of controlled conditions:

1. $CO_2$–free carrier air stream, flow 10 ± 0.5 liters per hour
2. Constant pressure in reaction vessel (745 mm. Hg)
3. Oil heating bath regulated so that reagent boils at a constant temperature; approximately 134° ± 0.3° C. oil bath temperature (dependent on radiation, size of flask, etc.)
4. Carrier air stream entry tube, 5–10 mm. above level of reagent in reaction flask

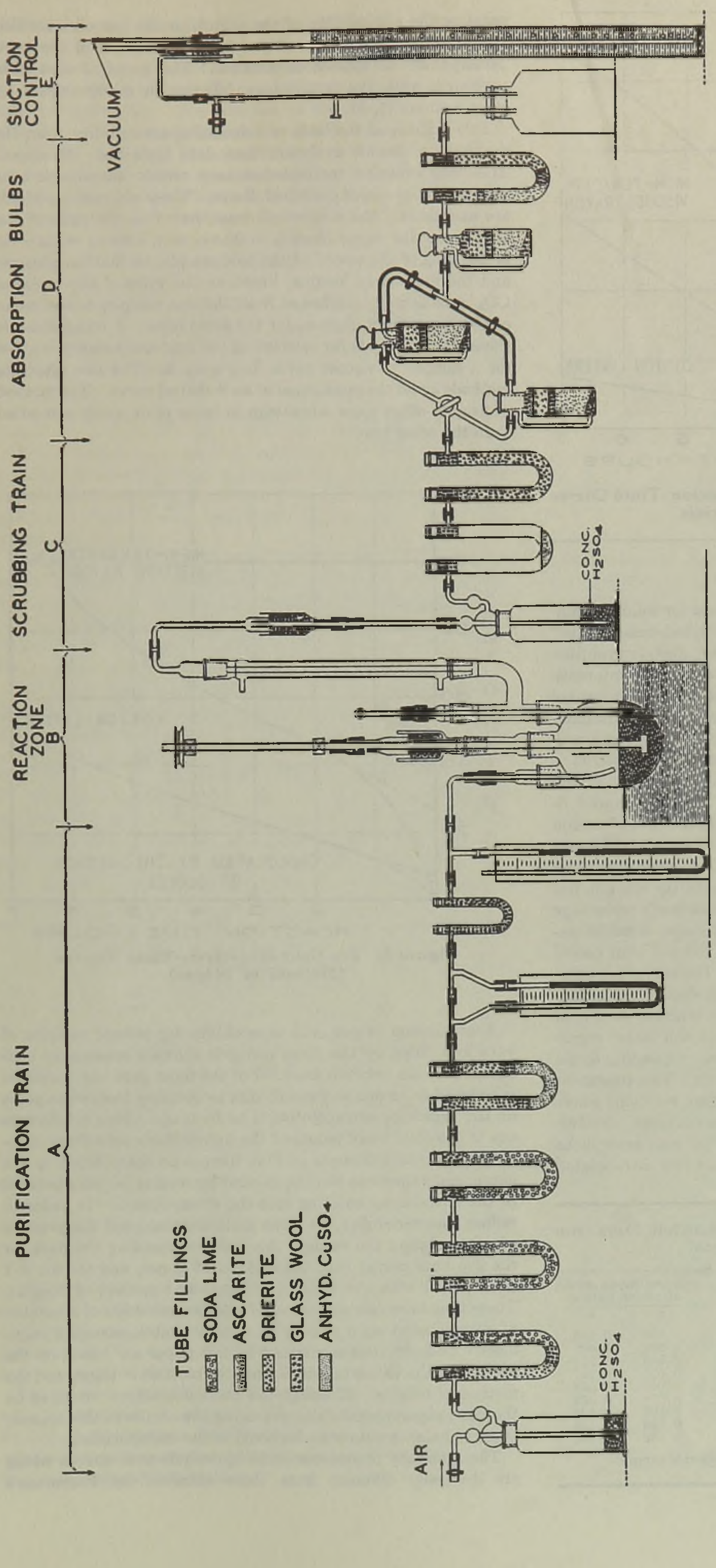

Figure 1. Hydrochloric Acid–Ferric Chloride Digestion Apparatus

5. Level of reagent in digestion flask 4–6 mm. above that of oil heating bath
6. Carborundum crystal boiling stones
7. Stirring by T-shaped mercury-seal glass stirrer (blade 8 × 15 mm.) at 350–400 r.p.m.

This carefully controlled set of conditions is necessary to ensure reproducibility of the carbon dioxide evolution rates.

Through parallel arrangement of the Nesbitt bulbs, measurement of the amounts of carbon dioxide evolved can be made over any desired period. The oil bath is heated electrically at such a rate that about 35 minutes are required to raise it from room temperature to a point high enough to promote boiling of the reagent. This period is used for sweeping the apparatus free of carbon dioxide (no significant amount of carbon dioxide is evolved from the sample during this heating-up interval). An alternate procedure may be employed (*8*) whereby the warming-up period is conducted in the absence of the sample. After the reaction mixture starts to boil, the sample can be introduced into the reaction vessel through a port in the side which is normally closed by a ground glass stopper. The usual practice is to measure the amount of carbon dioxide evolved for each half-hour interval after initial boiling of the reagent and to continue the half-hour measurements for a period of 2 hours; then measurements are made at intervals of one hour. Zero time for the reaction is considered to be the onset of boiling, and measurements are made over the following 7-hour period. In the case of glucose the carbon dioxide evolved is expressed as moles carbon dioxide per mole glucose; in the case of cellulosic materials, as moles carbon dioxide per mole of glucose which occurs as glucose anhydride in the sample. Typical carbon dioxide evolution curves for glucose, a representative high-tenacity rayon yarn, and commercial cotton linters are shown in Figure 2. Actual carbon dioxide evolution data for these materials are given in Table I.

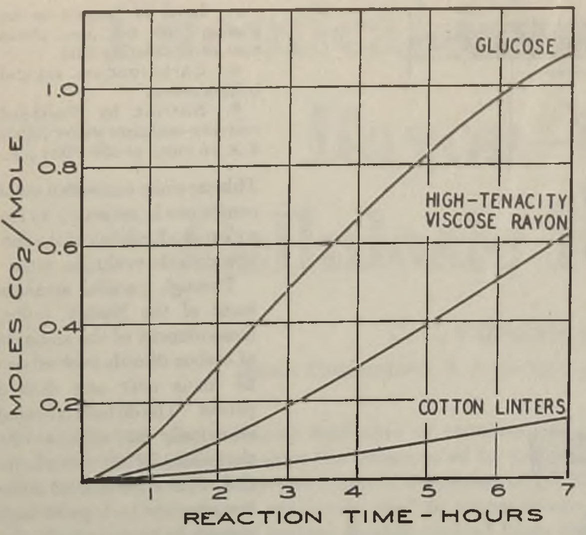

**Figure 2.** Typical Carbon Dioxide Evolution–Time Curves for Representative Materials

## TREATMENT OF DATA

The raw carbon dioxide evolution time data for cellulosic materials are converted to "percentage hydrolyzed–time curves" by obtaining the ratios of the rate of carbon dioxide evolution for the test sample to that for glucose at selected time intervals. The rates of carbon dioxide evolution are conveniently measured graphically from a plot of the carbon dioxide evolution time data. A plot of these ratios against time gives typical curves of a pronounced S-shape. This method of calculation will be referred to as the method of slopes. Figure 3 shows such curves for cotton linters and a commercial viscose rayon. The pronounced S-shape of the curves is a result of a decrease in the rate of carbon dioxide evolution for glucose (the reference material) which sets in after 5–6 hours of digestion. A similar decrease for cellulosic material does not take place in most cases until the reaction has proceeded for 7 hours or more. Actually, Nickerson's percentage hydrolyzed–time curves do not show this S-shape, since he extrapolated the linear 3–5 hour rate through the 5–7 hour period and disregarded the decreasing rate period. The curves are characterized by an initial region of relatively high slope which gradually falls off to one of lower slope as the most reactive portion of the material is consumed. Extrapolation of the latter region (2–5 hour period) to zero time gives a value corresponding to the amount of the most reactive part of the sample. This treatment is in accordance with the theory for consecutive reactions where two materials are present which react at different rates. Nickerson (*6*, *9*) calls this extrapolated value the "per cent amorphous cellulose" in the sample. We have designated this extrapolated value as the accessibility of the sample or the per cent accessibility because of the somewhat vague connotation of the word "amorphous" as applied to cellulose. This point of view is in agreement with the terminology followed in recent papers by other authors (*1*, *2*).

Two additional methods of calculating accessibility from the raw carbon dioxide evolution-time data have been developed. These are empirical methods but have certain advantages over the method of slopes described above. These alternate methods are as follows: the method of areas, based on the ratio of the area under the curve [from $t_0 = 0$ to $t_x = x$, where $t = (t_x - t_0)$ is the time of digestion] of the test sample, to that for glucose; and the method of heights, based on the ratio of the moles of $CO_2$/mole of anhydroglucose from the test sample, to the moles of $CO_2$/mole from glucose, for the same time. A comparison of these three methods for calculating per cent accessibility is given for a sample of viscose rayon in Figure 4. The two alternate methods avoid the production of an S-shaped curve. The method of heights offers some advantage in being more easily computed than the other two.

Table I. Typical Carbon Dioxide Evolution Data for Representative Materials

| Time, Hr. | Moles $CO_2$ per Mole of Sample[a]: Anhydrous glucose *a* | Anhydrous glucose *b* | High-tenacity viscose rayon *a* | High-tenacity viscose rayon *b* | Viscose rayon grade of cotton linters *a* | Viscose rayon grade of cotton linters *b* |
|---|---|---|---|---|---|---|
| 0.5 | 0.048 | 0.049 | 0.005 | 0.006 | 0.002 | 0.003 |
| 1.0 | 0.130 | 0.131 | 0.027 | 0.027 | 0.007 | 0.007 |
| 1.5 | 0.223 | 0.226 | 0.060 | 0.060 | 0.015 | 0.015 |
| 2.0 | 0.317 | 0.320 | 0.102 | 0.099 | 0.025 | 0.027 |
| 3.0 | 0.501 | 0.501 | 0.195 | 0.186 | 0.049 | 0.051 |
| 4.0 | 0.670 | 0.678 | 0.298 | 0.284 | 0.074 | 0.076 |
| 5.0 | 0.824 | 0.835 | 0.409 | 0.394 | 0.103 | 0.106 |
| 6.0 | 0.961 | 0.972 | 0.523 | 0.504 | 0.132 | 0.138 |
| 7.0 | 1.076 | 1.085 | 0.637 | 0.617 | 0.163 | 0.168 |

[a] Columns *a* and *b* represent check analyses on duplicate samples.

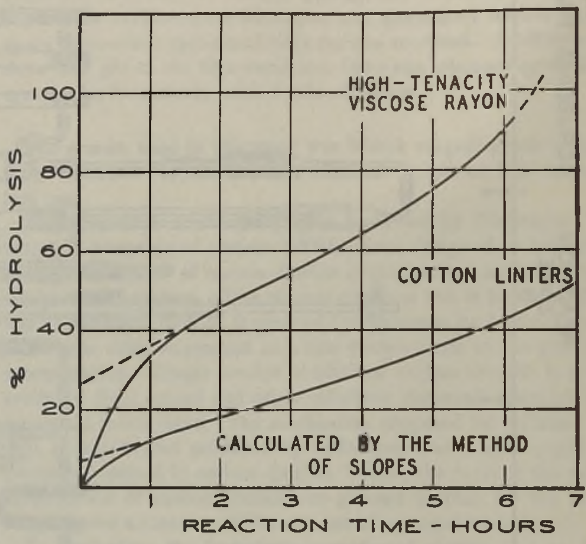

**Figure 3.** Per Cent Hydrolysis–Time Curves (Method of Slopes)

A calculation of per cent accessibility for several samples of yarn and pulps by the three methods shows a reasonably consistent relation between them. For the most part any variation is believed to be due to the difficulty in deciding from what point on the curve the extrapolation is to be made. This emphasizes one of the chief weak points of the hydrochloric acid–ferric chloride hydrolysis technique in that there is no sharp break in the curve, and values can thus be in error by several per cent because of the uncertainty entering into the extrapolation. In order to reduce this variability, we have arbitrarily adopted the practice of extrapolating the straight line best representing the data for the 2–5 hour period with the method of slopes, and for the 4–7 hour period with the method of areas and method of heights. These time intervals were selected after examination of a number of curves based on a variety of natural and regenerated celluloses. Accessibilities mentioned in this paper are based on the average of the values obtained from the method of slopes and the method of heights. Although the two calculations are based on the same experimental data, averaging the results in this manner tends to balance out errors involved in the extrapolations.

The alternate procedures yield hydrolysis-time curves which are decidedly different from those obtained by Nickerson's method of slopes. The plot (Figure 4) merely serves to illustrate the graphical methods followed in obtaining the intercept (accessibility), and as such is not necessarily concerned with which of the three methods of treating the raw data represents the actual degree of hydrolysis. The criticism of the method of slopes is solely from the point of view of the inconvenience of using this method in determining the accessibility or intercept. The curve for the method of slopes appears to give a close approximation of the true degree of hydrolysis of the cellulose (*6*). This method accordingly should be employed when it is desired to know the true degree of hydrolysis at any specified time; for example, samples could be compared on the basis of the amount of cellulose hydrolyzed in one hour.

All materials described in this report have a typical carbon dioxide evolution *vs.* time curve similar to that shown in Figure 2. To save space, the original experimental data are not given here but merely the derived accessibility values.

### MODIFICATIONS OF ANALYTICAL TECHNIQUE

When applying the method described by Nickerson (*7*) to replicate samples of a given material, large variations in the rate of carbon dioxide evolution were observed. These resulted in erratic accessibility values, particularly on samples of wood pulp or sheeted linters.

A detailed study of the procedure was made to find the chief factors causing the variability. The results obtained indicate that one or more of the reactions occurring during digestion has a high temperature coefficient. Accordingly, possible causes of variability in the temperature at which the reagent boils and variations due to local superheating were studied.

The use of glass beads, clay chips, or Carborundum crystals did not reduce superheating sufficiently to produce uniform results. Stirring has been found to reduce superheating materially and must be employed in order to obtain a satisfactory degree of reproducibility. Although Carborundum crystals were used in all experiments employing stirring, we have not established whether they are essential, and it may be that stirring alone is sufficient. Superheating in the absence of stirring is lowest for glucose (a homogeneous system), somewhat greater for regenerated cellulose fibers, and much higher for cotton cellulose and wood pulp. This difference between the pulps on the one hand and regenerated cellulose fibers on the other arises from the manner in which they react with the reagent. After a few minutes' contact with boiling hydrochloric acid–ferric chloride reagent, fibers of regenerated cellulose are dispersed into very fine particles which are circulated by the boiling liquid. Fibers from wood pulp or sheeted linters are not dispersed to the same extent and tend to accumulate at the bottom of the flask. Agitation by boiling alone does not keep these fibers away from prolonged contact with the hot walls of the flask; as a consequence, pronounced superheating, occasionally even charring, occurs.

In the absence of stirring, variations as high as 20–30% between cumulative carbon dioxide evolution values have been observed for materials such as pulps. The use of stirring has reduced the maximum variation to the order of 8–10% and normal variations to the order of 3–5%. Experimental data on three samples are included in Table I.

The minimum rate of stirring capable of reducing superheating to the level mentioned has not been determined. No change in the rate of carbon dioxide evolution has been found by varying the stirring rate over the range 375–575 r.p.m. For our work, therefore, the lower rate of stirring was adopted since less wear and tear on the equipment results at slow speeds.

For most of the tests, 500-ml. reaction flasks containing 150 ml. of reagent and 1.2–1.6 grams of sample were used. Increasing the size of the reaction vessel to 1000 ml. and doubling reagent volume and sample size showed no change in carbon dioxide evolution rate or accessibility level.

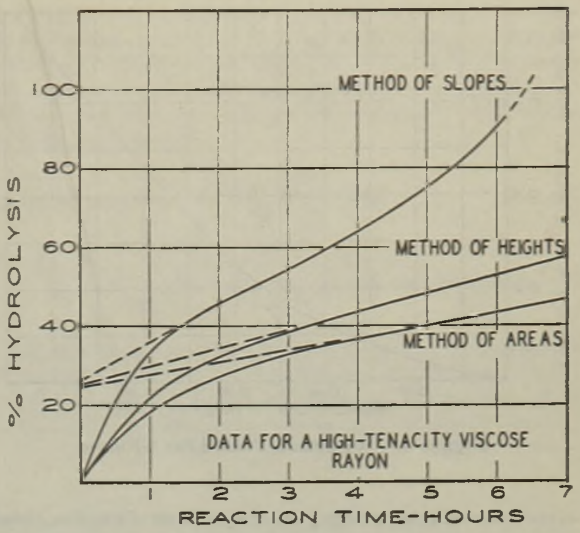

**Figure 4. Comparison of Methods of Determining Per Cent Accessibility**

In view of the high temperature coefficient and the fact that the reaction is carried out at the boiling point which is dependent on barometric pressure, experiments were performed to establish the effect on carbon dioxide evolution of normal atmospheric variations. For glucose the change in the amount of carbon dioxide evolved in the 7-hour reaction period amounts to about 0.04 mole carbon dioxide per mole glucose (about 4% variation) for a change in pressure of 1 cm. of mercury. Barometric pressure changes from day to day are of this magnitude; as a consequence, regulation of the pressure at some standard level is desirable in order to reduce variations from this source as much as possible. A pressure of 745 mm. of mercury has been selected as standard for the reaction as carried out in this laboratory. This pressure is somewhat below the prevailing barometric pressure and facilitates sweeping the carrier air stream through the apparatus by suction. The pressure coefficient under the conditions described has been found to be 0.375° C. per 1 cm. of mercury.

An alternate procedure which could be adopted would be to operate at a standard temperature of, say, 100° C. This would eliminate the dependence of the reaction temperature on barometric pressure and would, therefore, be more generally applicable in laboratories at different elevations.

The carbon dioxide evolution, expressed as the ratio of total number of moles of carbon dioxide produced during the 7-hour reaction period to the initial glucose concentration in moles, is not a constant but is dependent on the number of moles of glucose initially present in the system. Thus, strictly speaking, the reaction is not to be considered a pseudo unimolecular or first-order bimolecular reaction since the ratio for such a process should be a constant and not a function of changes in initial glucose concentration. In tests made to determine the extent of variation in this ratio with changes in initial glucose concentration, it was established that over an initial glucose concentration range of 0.025–0.075 mole per liter (0.6–1.8 grams per 150 ml.) the ratio decreases by 0.035 mole of carbon dioxide for each 0.001 mole increase in initial glucose concentration. Possible variation in our results on glucose, due to differences in sample size, has been eliminated by keeping the sample weight to a relatively narrow range (i.e., 1.4 to 1.6 grams).

Nickerson (*7*) describes a 0.4-hour induction period for glucose during which no indication of carbon dioxide evolution was observed. We have found this period to be characterized by the evolution of small amounts of carbon dioxide which are produced at a steadily increasing rate. Figure 5, a plot of carbon dioxide

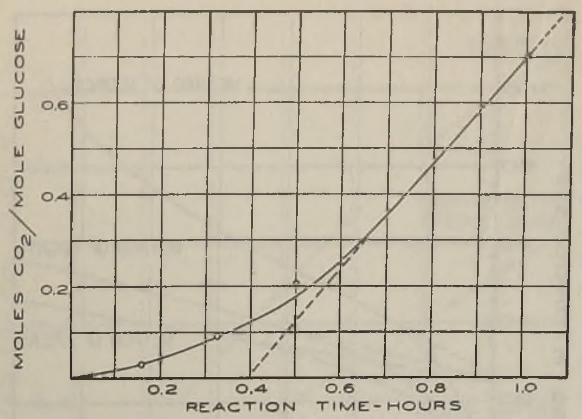

**Figure 5. Induction Period for Glucose**

evolution from glucose during the first one hour of reaction, shows that small amounts of carbon dioxide are evolved during this period. The intercept of the broken line (an extrapolation of the later part of the curve) with the time axis corresponds to the 0.4-hour induction period described by Nickerson. Presumably this induction period corresponds to the formation of an intermediate upon which the production of carbon dioxide depends. The induction period becomes less prominent with samples which produce less carbon dioxide. Thus, with sheeted linters an induction period is not distinguishable, as the amounts of carbon dioxide evolved blend smoothly into the following slow rate region.

### GLUCOSE CARBON EVOLVED AS CO$_2$

While it is assumed that cellulose is hydrolyzed to glucose and the latter oxidized with the evolution of carbon dioxide, the specific nature of the reaction has not been established. In order to secure information on this point, it appeared desirable to determine to what extent the glucose molecule was oxidized; i.e., was one or more of the six carbon atoms oxidized?

An attempt was made to resolve the carbon dioxide evolution data according to the theory of step reactions of the first order. This treatment was not successful due to difficulty in measuring the concentration of glucose in the presence of ferric chloride.

Another approach was to allow the reaction to go to completion (48 to 50 hours) and calculate moles of carbon dioxide given off. As Figure 6 shows, the molar amounts of carbon dioxide evolved do not correspond to a whole number. The rate seems to drop off appreciably after 10 hours. The change in carbon dioxide evolution rate suggests a fast initial reaction covering the first 10-hour period and yielding 1 mole of carbon dioxide per mole of glucose. The latter low rate period suggests the continued slow oxidation of some residue from the initial reaction to give additional amounts of carbon dioxide. Just what reactions take place are not known. In a similar run, except that the temperature was not carefully controlled, a value of 2.1 moles of carbon dioxide was obtained. Evidence of carbonization in the residues from the 50-hour runs suggests some reaction yielding elemental carbon, in competition with the oxidative steps producing carbon dioxide.

### OBSERVED ACCESSIBILITY VALUES

**Wood Pulps and Cotton Linters.** It has been felt that the accessibility determination might throw some light on the characteristics of cotton linters and wood pulps used in rayon manufacture which are not revealed by the normal tests, such as alpha, beta, and gamma determinations, solubility in ether and caustic, amount of impurities, viscosity, etc. The measurement of per cent accessibility on ten lots of cotton linter sheets from a single source showed a small difference in accessibility between the samples. The average found was 5.3% and the total range 4.5–6.0%.

In general, a decrease in the accessibility value parallels an increase in the alpha cellulose of the raw material. This general relation is shown in Table II. This decrease in accessibility may arise from the somewhat smaller amounts of relatively low-molecular-weight materials, such as beta and gamma cellulose (particularly, pentosans) in the high-alpha materials. Actual experiment has shown that xylose, a pentosan, evolves carbon dioxide at rates higher than cellulose or even glucose; as a result, an increase in accessibility should occur for this reason when materials of this type are present. In all instances, for the materials examined, commercial rayon-grade wood pulps show a higher accessibility than cotton linters.

Table II. Accessibility of Rayon-Grade Wood Pulps and Cotton Linters to Hydrochloric Acid–Ferric Chloride Attack

| Description | % Alpha Cellulose | % Accessibility |
|---|---|---|
| Wood pulp from beech | 88.5–89.0 | 11.5 |
| Wood pulp from southern pine | 93 | 10.0 |
| Wood pulp from western hemlock | 91.5 | 9.0 |
| High-alpha wood pulp from southern pine | 94.5–95.0 | 7.5 |
| Cotton linters (degree of polymerization approx. 1000) | 98.5 | 5.3 |

Table III. Accessibility of Special Cotton Linters and Wood Pulp Samples to Hydrochloric Acid–Ferric Chloride Attack

| | Av. Degree of Polymerization | % Accessibility |
|---|---|---|
| Effect of mercerization and aging | | |
| Cotton linters | 1000 | 5.3 |
| Cotton linters alkali cellulose after shredding | 850 | 14.5 |
| Cotton linters alkali cellulose after shredding and aging | 610 | 11.0 |
| Effect of activation treatment | | |
| Cotton linters, dried from water by solvent extn. with CH$_3$OH followed by C$_6$H$_6$ | .. | 7.5 |
| High-alpha wood pulp from southern pine | .. | 7.5 |
| High-alpha wood pulp from southern pine, treated with cold caustic of below mercerizing strength | .. | 14.5 |
| High-viscosity cotton linters | 1440 | 5.0 |

Table III gives the effects of special treatments on the accessibility of cotton linters and wood pulps. It is interesting to note the difference in accessibility between alkali cellulose before and after aging, during which the D.P. (degree of polymerization) was lowered from approximately 850 to approximately 610 glucose anhydride units. A small increase in accessibility as a result of alkali cellulose aging should be expected because of the formation of some fragments of relatively low molecular weight. The total changes in accessibility during mercerization cannot be measured because some of the products formed (beta and gamma cellulose) are lost during purification. Purification is essential, otherwise the residual caustic will interfere with the accessibility determination. It is assumed that the observed increase in accessibility brought about by mercerization can arise either from swelling of the lattice structure or from the formation of shorter chain lengths, but we do not have direct experimental evidence as to which of these effects is greater.

Generally speaking, our tests indicate that accessibility is not much affected by changes in average degree of polymerization over a reasonably wide range. In fact, cotton linters of 1440 D.P. have practically the same accessibility as a sample with a D.P. of 1000. It appears, therefore, that increases in accessibility during mercerization may arise primarily from changes brought about by swelling as distinct from shorter chain lengths.

Goldfinger, Mark, and Siggia (3) find an increased accessibility in the behavior of cotton linters to periodic acid solution when the cellulose is dried by solvent extraction with methanol followed by benzene instead of being dried directly from water. Our experiments indicate that a small increase in accessibility toward hydrochloric acid–ferric chloride attack is also observed. Approximately a twofold increase in accessibility of a high-alpha wood pulp from southern pine is brought about by preswelling in cold 10% caustic (under conditions which do not permit mercerization). This method of activating cellulose was recently used by Assaf, Haas, and Purves (1). The level of accessibility of the cold-alkali-treated wood pulp is in the range observed for mercerized cotton linters although the samples were treated under conditions markedly different in swelling.

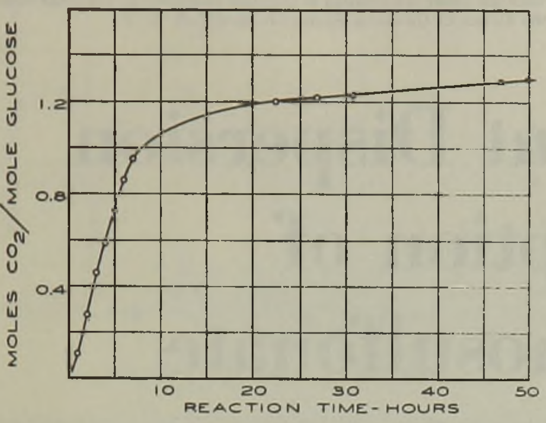

**Figure 6. Carbon Dioxide Evolution from Glucose over a 50-Hour Reaction Period**

Regenerated Cellulose Yarns. Wide variations in the accessibilities of regenerated cellulose yarns exist. Values for typical regenerated cellulose yarns are shown in Table IV. For most of these materials the accessibility increases with decreasing crystallinity. This is in line with Nickerson's hypothesis (4, 5) that materials have a high accessibility due to the presence of a large amount of "amorphous cellulose", and, on the other hand, that materials with a low accessibility are characterized by the presence of large amounts of relatively nonreactive or crystalline cellulose. Delustering by the addition of pigments or oils to the viscose prior to spinning does not affect accessibility. It should be noted that a textile yarn which we know to have only moderate strength has about the same accessibility as do certain high-strength rayons. Since, in many cases, strength is gained through increasing the orientation of the micelles within the filament, this behavior suggests that orientation to the extent present in these yarns does not play a significant part in reactivity of cellulose to attack by hydrochloric acid–ferric chloride.

Table IV. Accessibility of Regenerated Cellulose Yarns to Hydrochloric Acid–Ferric Chloride Attack

| Type of Rayon | Dry Yarn Strength G. per denier | Dry Yarn Strength G. per grex | Elongation, % | Accessibility, % |
|---|---|---|---|---|
| High tenacity-low elongation, viscose process | 4.9 | 4.4 | 7.4 | 15.0 |
| High tenacity, deacetylated cellulose acetate | 4.2 | 3.8 | 7.2 | 16.5 |
| Textile, delustered, viscose process | 1.8 | 1.6 | 17.8 | 27.0 |
| Textile, bright, viscose process | 1.8 | 1.6 | 18.6 | 27.0 |
| High tenacity, commercial tire corn yarn, viscose process | 3.7 | 3.4 | 9.7 | 27.0 |
| High tenacity (exptl.), viscose process | 3.9 | 3.5 | 10.8 | 31.5 |

To get a more positive picture of the relation between accessibility and the amorphous-crystalline distribution, x-ray diffraction studies were carried out. H. G. Ingersoll of the Chemical Department, E. I. du Pont de Nemours & Company, made the x-ray studies which we are reporting. Equatorial photometer measurements of the interference patterns from x-ray diffraction pictures were taken and "crystallinity numbers" calculated by the following formula:

$$\text{crystallinity number} = \left[\frac{\bar{I}_1 - \bar{I}_M}{\bar{I}_1}\right] \times 100$$

where $\bar{I}_1$ = av. intensity of 101 interference
$\bar{I}_M$ = av. intensity of minimum between 101 and the $10\bar{1}$ interference

Crystallinity numbers calculated in this way were plotted against the accessibility values determined on the same material; Figure 7 shows a reasonably good correlation with accessibility. It is admitted that the x-ray parameter termed "crystallinity number" is not an absolute value. It has been used merely to secure a relative rating. This is a preliminary grading since no corrections have been made for the effect of such factors as orientation, crystal size, crystal distortion, the presence of small amounts of native cellulose, etc. However, if we assume that the degree of order measured by this parameter is primarily dependent on the degree of crystallinity of the cellulose, then the hypothesis that accessibility is primarily a function of the amount of amorphous or unorganized cellulose present is strongly supported. Although the two methods are in general agreement, they are of such an empirical nature that no idea of the absolute amount of crystalline or amorphous cellulose in the sample can be drawn. In some cases, samples with the same accessibility have different crystallinity numbers, and the reverse can also be observed on the chart; this behavior confirms the empirical basis of the determination.

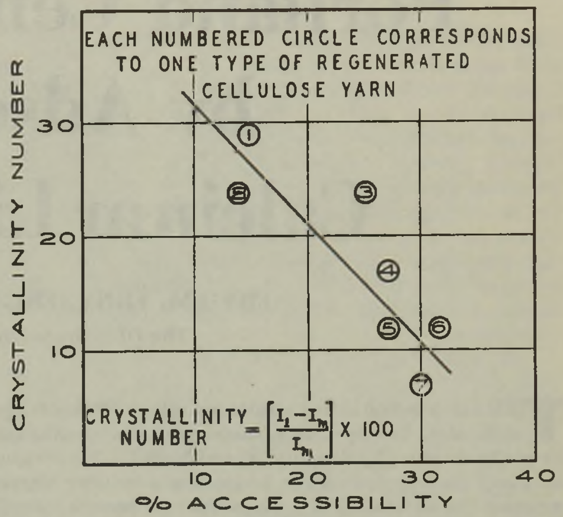

**Figure 7. Hydrochloric Acid–Ferric Chloride, Accessibility *vs.* Crystallinity Number for Regenerated Cellulose Yarns**

## SUMMARY

1. Modifications to the hydrochloric acid–ferric chloride hydrolytic and catalytic oxidation method developed by Nickerson (7) have included changes designed to reduce superheating and minimize differences in boiling point arising from changes in barometric pressure. A reduction in variability and an improvement in reproducibility are obtained with the modified apparatus.

2. Alternate methods for calculating accessibility to attack by hydrochloric acid–ferric chloride have been suggested.

3. A detailed study of the reaction reveals that it is characterized by an induction period in which small amounts of carbon dioxide are produced at a steadily increasing rate, suggesting the formation of an intermediate on which the production of carbon dioxide is dependent. The reaction between hydrochloric acid–ferric chloride and glucose is not complete in 50 hours. An abrupt change in rate at about one mole carbon dioxide per mole glucose, occurring after 10 hours of reaction, suggests the completion of a comparatively rapid reaction evolving one mole of carbon dioxide.

4. The accessibility of cotton linters and wood pulps, in most cases, decreases with increasing alpha cellulose content of the pulp.

5. Accessibility of regenerated cellulose yarns decreases with increasing crystallinity number, as calculated from intensity measurements of x-ray diffraction patterns. To a certain degree this confirms the contention that the accessibility measurement is chiefly a measure of amorphous cellulose.

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# Portland Cement Dispersion by Adsorption of Calcium Lignosulfonate

FRED M. ERNSBERGER AND WESLEY G. FRANCE
*The Ohio State University, Columbus 10, Ohio*

**The results of turbidity tests on portland cements suspended in an aqueous medium, with and without addition of calcium lignosulfonate, as obtained with the Wagner turbidimeter, show that the addition agent disperses the suspended cement particles. In the tests reported, the degree of increase in turbidity for two types of portland cement in an aqueous medium is shown to be a function of the amount of adsorbed dispersing agent. It may be concluded that the mechanism of dispersion involves the positive adsorption of lignosulfonate anions by the cement particles. The determination of an adsorption isotherm for calcium lignosulfonate and portland cement suspended in water is described; data are given for a typical cement.**

THE lignin derivative from waste sulfite liquor (calcium lignosulfonate), discovered as a plasticizing and dispersing agent for portland cement by Scripture (*6*) and Mark (*3*), has been used for many years in the cement and concrete industry where it improves the workability of the concrete mix, permits reduction of the water-cement ratio, and leads to improved strength and to freezing, thawing, and sulfate durability (*1, 2, 4, 5*). The calcium lignosulfonate used in this investigation is a mixture of the neutral calcium-magnesium salts of alpha and beta lignosulfonic acids, which is a commercial product and contains impurities. It has been suggested (*5*) that the above effects, particularly the reduction in water-cement ratio, result from increased dispersion of the portland cement in the presence of lignosulfonates; that is, agglomerates of cement particles do not form in the presence of a dispersing agent, and water which otherwise would have been trapped within the agglomerate is free to become a part of the mixing or placing water.

The purpose of this investigation was to study the effect of calcium lignosulfonate on cement-water suspensions and to determine the function of calcium lignosulfonate in cement dispersion.

Examination of a dilute cement-water suspension under the microscope reveals many more discrete particles, particularly small particles, when the water medium contains about 0.1% of calcium lignosulfonate. A striking manifestation of the increased dispersion is the vigorous Brownian motion observed in the presence of the calcium lignosulfonate. A cement suspension in pure water contains very few discrete particles small enough to exhibit this phenomenon.

### TURBIDIMETER MEASUREMENT

A method for measuring the degree of dispersion of cement-water suspensions is difficult to devise. The method used here involves the application of Stokes' law to falling cement particles in a water medium, with and without calcium lignosulfonate, using the Wagner turbidimeter (*7*). It is necessary to assume only that the measured specific surface of a cement is a function of the state of dispersion of the cement suspension used in the measurement.

The technique adopted is similar to A.S.T.M. Designation C115, except that water is used for the suspending medium instead of kerosene. In the preparation of the suspension the cement is agitated in the calcium lignosulfonate solution for 2 minutes instead of 1 minute because this allows better opportunity for the adsorption equilibrium to be established. It is also necessary to compute from Stokes' law the time in seconds, at a given temperature, when the microampere readings are to be taken for the various particle sizes from 60 down to 7.5 microns. The light-absorbing effect of the equilibrium concentration of calcium lignosulfonate present is taken into account in adjusting the initial light intensity at 100 microamperes. The results of these tests (Table I) reveal that the use of calcium lignosulfonate increases the turbidity of the cement-water suspensions, as indicated by the increase in specific surface in the water medium.

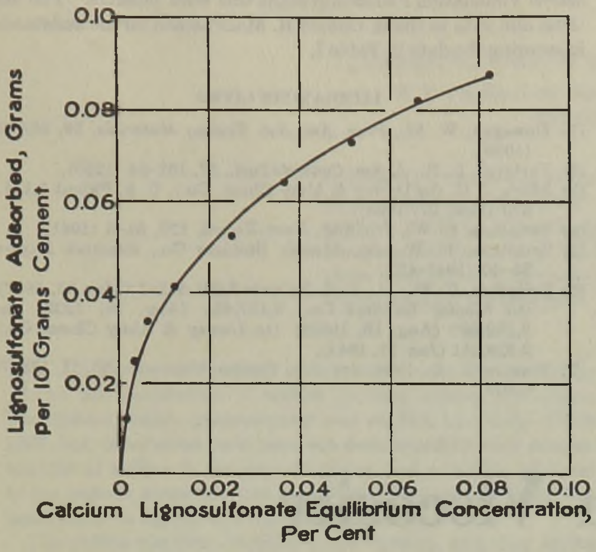

Figure 1. Adsorption Isotherm

The increase in turbidity produced by calcium lignosulfonate was readily apparent from visual examination of the undispersed and dispersed suspensions before and after each test. Although the maximum amount of dispersion secured in these tests was that obtained with 0.5 gram of calcium lignosulfonate per 100 grams of cement, the most effective quantities appear to be in the range 0.2 to 0.4 gram of dispersing agent per 100 grams of cement. The Wagner specific surface data for these cements, as measured in kerosene and dispersed with oleic acid, are included in Table I.

While the effect of hydration may have influenced the results of the Wagner turbidimeter tests, it is believed that there were no serious errors from this source. Careful adherence to a rigid time schedule (10 minutes ± 10 seconds, including brushing period) eliminates relative errors due to the progress of hydration.

TABLE I. SPECIFIC SURFACE OF PORTLAND CEMENT SUSPENDED IN WATER, WITH AND WITHOUT CALCIUM LIGNOSULFONATE

| Ca Lignosulfonate Adsorbed, G./100 G. Cement[a] | Av. $I_{60}$, Microamp. | Av. 2 Log $I_{60}$ | Av. Transmittancy Constant (1 G. Basis) | Av. Sp. Surface, Sq. Cm./Gram[b] | Apparent % Increase in Surface Dispersed over Undispersed |
|---|---|---|---|---|---|
| Type I Cement: 90% Passing 325-Mesh Sieve; Sp. Surface in Kerosene, 1690 Sq. Cm./Gram | | | | | |
| None | 26.8 | 0.572 | 603 | 1150 | .. |
| 0.2 | 24.5 | 0.611 | 740 | (1505) | 31 |
| 0.3 | 23.2 | 0.635 | 743 | 1570 | 37 |
| 0.4 | 21.3 | 0.672 | 751 | (1685) | 47 |
| 0.5 | 20.7 | 0.684 | 748 | 1705 | 48 |
| Type III Cement: 100% Passing 325-Mesh Sieve; Sp. Surface in Kerosene, 2590 Sq. Cm./Gram | | | | | |
| None | 12.5 | 0.903 | 605 | 1820 | .. |
| 0.2 | 11.0 | 0.959 | 720 | (2300) | 26 |
| 0.3 | 10.1 | 0.996 | 723 | 2400 | 32 |
| 0.4 | 8.6 | 1.065 | 723 | 2575 | 41 |
| 0.5 | 8.2 | 1.086 | 727 | 2630 | 44 |

[a] Approximate values obtained from adsorption equilibrium data by calculating the total amount of calcium lignosulfonate needed, for the system used, to satisfy the amount adsorbed per 100 grams of cement plus the amount required for equilibrium.

[b] Calculated from individual transmittancy constant; each value is the average of two or more determinations, except those in parenthesis which are single tests.

TABLE II. PORTLAND CEMENT-CALCIUM LIGNOSULFONATE ADSORPTION DATA

| Ml. of 1.5% Ca Lignosulfonate | Ca Lignosulfonate Equilibrium Soln. | | | | Lignosulfonate Adsorption, G./10 G. Cement |
|---|---|---|---|---|---|
| | Optical density | Concn., % | Concn. obtained graphically, % | Initial concn., % | |
| 0 | 0.000 | 0.0000 | 0.000 | 0.000 | 0.000 |
| 1 | 0.008 | 0.0022 | 0.001 | 0.010 | 0.013 |
| 2 | 0.012 | 0.0033 | 0.003 | 0.020 | 0.025 |
| 3 | 0.022 | 0.0061 | 0.007 | 0.030 | 0.035 |
| 4 | 0.046 | 0.0128 | 0.013 | 0.040 | 0.041 |
| 6 | 0.088 | 0.0247 | 0.025 | 0.060 | 0.053 |
| 8 | 0.133 | 0.0373 | 0.037 | 0.080 | 0.064 |
| 10 | 0.178 | 0.0499 | 0.051 | 0.100 | 0.073 |
| 12 | 0.237 | 0.0662 | 0.066 | 0.120 | 0.081 |
| 14 | 0.292 | 0.0817 | 0.081 | 0.140 | 0.088 |

### MECHANISM OF DISPERSING ACTION

Dispersion of small particles in aqueous suspensions is usually considered to be due to the mutual repulsion of electrical fields of the particles. That this mechanism is operative in the case of cement-water suspensions dispersed by calcium lignosulfonate has been demonstrated by observing under the microscope the electrophoretic migration of suspended cement particles. Cement particles suspended in distilled water show no tendency to migrate toward either electrode; in fact, the particles agglomerate and settle out so rapidly it is difficult to find one which can be observed. On the other hand, cement particles suspended in calcium lignosulfonate solution show a readily observable migration toward the anode. It may therefore be concluded that cement particles acquire a negative potential in calcium lignosulfonate solution, leading to the formation of a more stable suspension.

The negative potentials of the cement particles are attributable to the adsorption of lignosulfonate anions. The existence of such ions has been demonstrated by a simple electrophoresis experiment. When an aqueous solution of calcium lignosulfonate is placed in an electrophoresis cell and a potential applied, the brown lignosulfonate complex moves toward the anode and forms a sharp boundary with the colorless solution surrounding the cathode. In the cathode solution a precipitate of metallic hydroxide appears. Obviously the lignin salt is a colloidal electrolyte which ionizes in solution to give metallic cations and lignosulfonate anions.

To show that lignosulfonate anions are positively adsorbed by the cement particles requires a more elaborate technique. For this purpose a spectrophotometric method was used to determine an adsorption isotherm for a typical normal portland cement.

### DETERMINATION OF ADSORPTION ISOTHERM

The equilibrium solutions needed to establish the cement–calcium lignosulfonate isotherm are made by taking predetermined amounts of 1.500% calcium lignosulfonate solution and diluting each portion in a volumetric flask to 150 ml. with distilled water. Into each of these known concentrations of calcium lignosulfonate, 10 grams of portland cement are added with vigorous mechanical stirring for 5 minutes (previous tests showed equilibrium is established in less than 5 minutes). The suspensions are then filtered and a portion of each filtrate, which is acidified with hydrochloric acid to prevent carbonate formation, is taken for spectrophotometric analysis. In the absence of a satisfactory chemical method for determining very small amounts of calcium lignosulfonate, the spectrophotometric method is used.

The optical density of each equilibrium concentration of calcium lignosulfonate is measured at a wave length of 410 mμ, using a Coleman Model 10 spectrophotometer. From a calibration curve, concentration values are then taken which correspond to the measured optical densities:

$$\text{optical density} = \log (100/T)$$

where $T$ = transmission, %

In securing the calibration curve, it is necesssary to measure the optical densities of a series of solutions of known calcium lignosulfonate content, which have been individually adjusted to approximately the same pH as the acidified equilibrium solutions. The calibration curve is then a graphic relation between observed optical densities and known calcium lignosulfonate concentrations. A typical set of cement–calcium lignosulfonate adsorption data is shown in Table II, where different concentrations of calcium lignosulfonate solutions were used with a normal portland cement.

The equilibrium solution concentration values in column 3 are plotted against the values in column 1, and the best curve is drawn through the points. Equilibrium concentration values are then taken from the curve and are shown in column 4. The adsorption in grams of lignosulfonate per 10 grams of cement is calculated by subtracting the equilibrium solution concentration obtained from the curve from the initial concentration and multiplying by 1.5 (column 6). The adsorption isotherm (Figure 1) represents the relation between the grams of lignosulfonate adsorbed per 10 grams of cement and the equilibrium concentrations of calcium lignosulfonate (values in column 6 *vs.* values in column 4).

### ACKNOWLEDGMENT

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# Molecular Refraction–Viscosity Constant Nomograph

R. T. LAGEMANN
*Emory University, Emory University, Georgia*

SOUDERS (*3*) showed that for organic liquids there exists a viscosity-constitutional constant $I$ which is defined as

$$I = \frac{M}{d}\left\{\log_{10} \log_{10} \eta + 2.9\right\}$$

where $\eta$ = viscosity, millipoises; $d$ = density, grams per cc.; $M$ = molecular weight

Values of $\eta$ and $d$ are taken at the same temperature. Recently (*2*) it was pointed out that Souders' $I$ is a linear function of the molecular refraction, $R$, which is defined as

$$R = \frac{n^2 - 1}{n^2 + 2}\,\frac{M}{d}$$

where $\eta$, the refractive index, and $d$ must be measured under the same conditions. Thus it is possible to determine the viscosity of a liquid from its refractive index which is easy to measure and for which a large amount of data is available.

The nomograph shown by Figure 1 provides a convenient way for estimating Souders' $I$ from the mole refraction. By aligning the mole refraction value with the series number of the compound, the corresponding value of $I$ may be read from the right-hand scale. When values of the viscosity and the refractive index are to be connected with values of $I$ and $R$, respectively, use may be made of two nomographs designed by Davis (*1*).

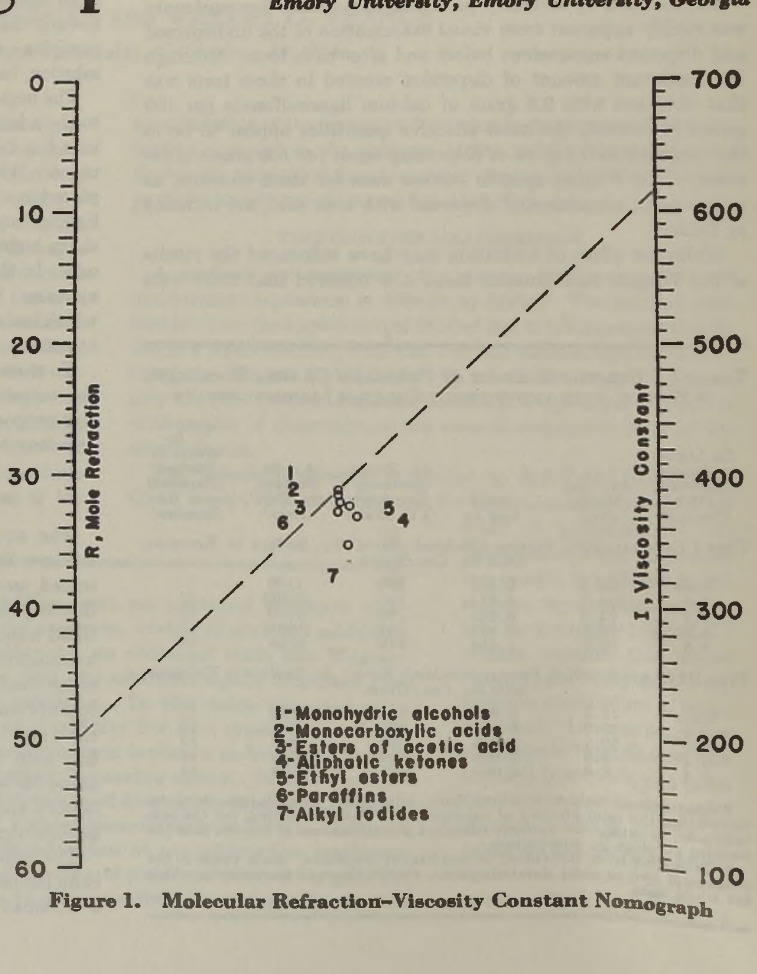

Figure 1. Molecular Refraction–Viscosity Constant Nomograph

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# Solubility Data for the System Aniline-Toluene-Water

JULIAN C. SMITH AND ROGER E. DREXEL

*E. I. du Pont de Nemours & Company, Inc.*
*Wilmington, Del.*

**Solubility data are presented for the ternary system aniline-toluene-water at 25° C. The distribution between organic and aqueous phases is correlated by an empirical exponential function, which fits the data more closely than a hyperbolic function of the type developed by Varteressian and Fenske (8).**

IN THE course of a process investigation, data were necessary on the distribution of aniline between toluene and water. The system aniline-toluene-water was studied by Riedel (*5*) in 1906, but distribution data were not determined for high concentrations of aniline in the organic phase, and solubility of water in the organic phase was not measured. The present study was undertaken to supply this missing information.

The aniline was twice distilled under vacuum, and after drying over solid sodium hydroxide, had a specific gravity of $d_4^{25}$ 1.0156, and a refractive index at 25° C. of 1.5840. The toluene was fractionated through a short packed column, and the fraction boiling between 110.6 and 111.0° C., at 772 mm. of mercury, used in the subsequent experiments. It had a specific gravity of $d_4^{26}$ 0.8616 and a refractive index at 25° C. of 1.4928. Distilled water from the laboratory was used.

Limiting solubilities in the organic phase were determined by pipetting known amounts of aniline and toluene into small glass-stoppered Erlenmeyer flasks to give a total volume of about 30 cc. Water was then added until a slight turbidity remained after thorough shaking. Any small excess of water was allowed to separate, and the organic phase was carefully sampled with a pipet. The samples were analyzed for water, using the Karl Fischer method. The refractive index was determined with an Abbe refractometer. Data so obtained were plotted as shown in Figure 1, and solubility of water in other known mixtures of aniline and toluene was obtained from the refractive index. Solubilities in the water layer were determined by titrating known mixtures of aniline and water with toluene from a microburet. With 100 cc. of aniline and water, however, such small quantities of toluene were involved that this method merely showed the solubility of toluene to be below 0.06% in all cases.

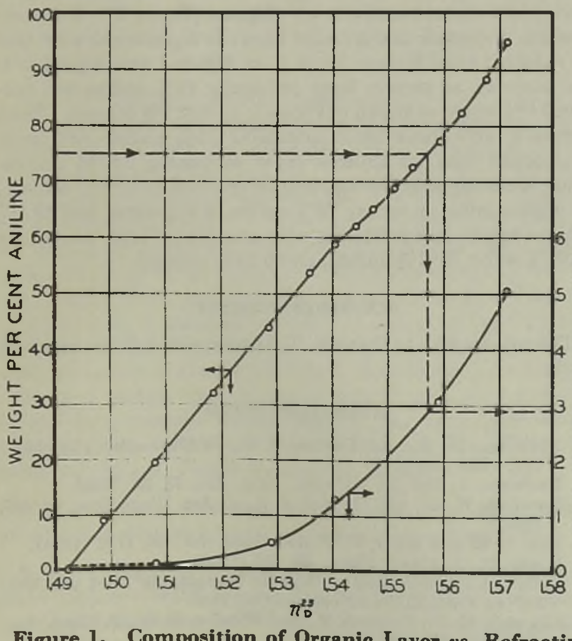

Figure 1. Composition of Organic Layer *vs.* Refractive Index at 25° C.

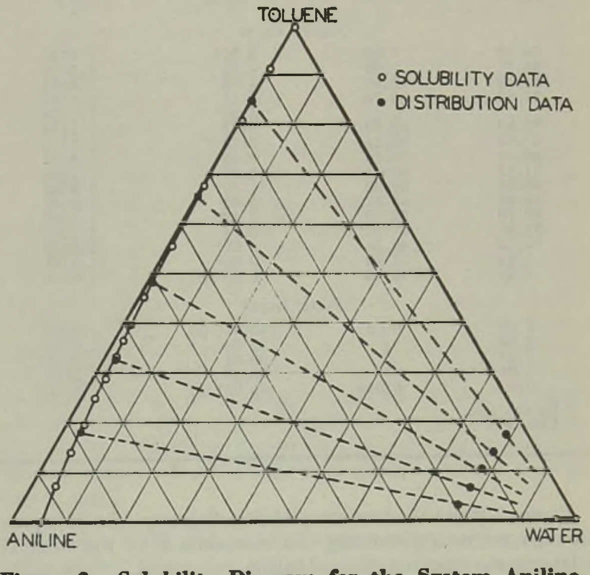

**Figure 2. Solubility Diagram for the System Aniline-Toluene-Water at 25° C.**

Data on limiting solubilities and corresponding refractive indices at 25° C. are given in Table I and plotted in Figure 1. Solubilities of water in toluene, toluene in water, and aniline in water were taken from Seidell (*6*). The solubility of water in aniline at 25° C. was determined analytically. The present value agrees with the one given by Appelbey and Davies (*1*), but not

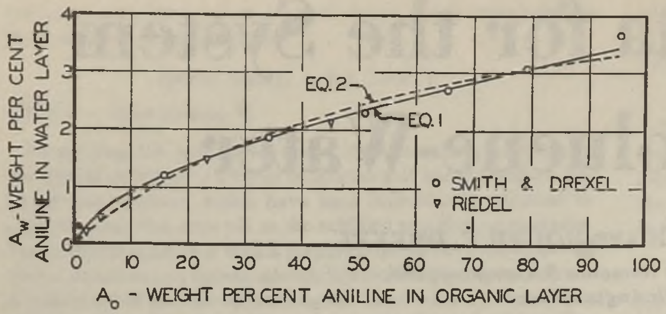

**Figure 3. Distribution of Aniline between Toluene and Water at 25° C.**

with those of Sidgwick, Pickford, and Wilsdon (*7*), or Hill and Macy (*4*). All the previous determinations were synthetic.

An inversion of the position of the two layers occurs at about 90% aniline in the organic phase. At concentrations of aniline above 90%, the organic layer is the heavy phase; at lower concentrations of aniline, the water layer is the heavy phase.

The tie lines were determined by making up known mixtures of aniline, toluene, and water in the area of heterogeneity, having a total volume of about 250 cc. The mixtures were thoroughly shaken and allowed to settle. The refractive index of each layer was then determined, and the water layer analyzed for aniline, using nitrous acid and starch iodide test paper. From these analyses and the graphs given in Figure 1, the distribution data given in Table II were calculated.

Table I. Limiting Solubilities at 25° C.

| Composition, Weight % | | | |
|---|---|---|---|
| Aniline | Toluene | Water | $n_D^{25}$ |
| | | Organic Layer | |
| 94.95 | 0.00 | 5.05[a] | 1.5712 |
| 88.21 | 7.49 | 4.30 | 1.5675 |
| 82.38 | 13.99 | 3.63 | 1.5632 |
| 77.18 | 19.68 | 3.14 | 1.5594 |
| ... | .... | 3.07[a] | 1.5590 |
| 72.76 | 24.72 | 2.52 | 1.5540 |
| 68.63 | 29.14 | 2.23 | 1.5512 |
| 65.01 | 33.14 | 1.85 | 1.5473 |
| 61.72 | 36.71 | 1.57 | 1.5444 |
| 58.78 | 39.93 | 1.29[a] | 1.5403 |
| 53.63 | 45.51 | 0.86 | 1.5358 |
| 43.79 | 55.73 | 0.48[a] | 1.5287 |
| 31.93 | 67.83 | 0.24 | 1.5185 |
| 19.05 | 80.86 | 0.09[a] | 1.5078 |
| 8.61 | 91.33 | 0.06 | 1.4987 |
| 0.00 | 99.95 | 0.05 (*6*) | 1.4923 |
| | | Water Layer | |
| 3.66 | 0.00 | 96.34 (*6*) | 1.3400 |
| 2.96 | [b] | 97.04 | 1.3383 |
| 1.99 | [b] | 98.01 | 1.3362 |
| 1.01 | [b] | 98.99 | 1.3340 |
| 0.00 | 0.049 | 99.951 (*6*) | 1.3320 |

[a] By analysis.
[b] Less than 0.06%.

Figure 2 shows the ternary solubility diagram. Tie lines pass through points representing the composition of the original mixtures, showing that material balances were good. The equilibrium concentration of aniline in the water layer is plotted against its concentration in the organic layer in Figure 3. The data given by Riedel (*5*) are included for comparison.

## CORRELATION OF DATA

There is excellent agreement between both sets of data. The distribution of aniline between the two layers is defined closely by the equation:

$$A_w = 0.239\,(A_o)^{0.584} \qquad (1)$$

where $A_w$ = percentage of aniline in water layer
$A_o$ = percentage of aniline in organic layer

The solid line in Figure 3 represents the distribution as calculated from Equation 1. This equation applies, with a maximum error of 2.5%, between 10 and 90% aniline in the organic phase. A fair correlation of data is obtained by the equation:

$$A_w = \frac{0.0881\,A_o}{1 + 0.0159\,A_o} \qquad (2)$$

which is the type developed by Varteressian and Fenske (*8*) for the system aniline–methylcyclohexane–*n*-heptane. Equation 2 is represented by the dashed line in Figure 3.

The distribution data of Varteressian and Fenske obey exponential equations similar to Equation 1 about as well as they do hyperbolic equations similar to Equation 2. Neither present data nor the data of Varteressian and Fenske obey the distribution equation given by Bachman (*2*), or the mass-law type of equation given by Bancroft and Hubard (*3*), both of which are empirical, but which apply to a large number of ternary systems composed of two miscible pairs of liquids. Apparently these equations do not generally apply to systems consisting of two immiscible pairs. Relatively few systems of this type have been studied, and no general correlation has been found.

Table II. Distribution Data at 25° C.

| Original Mixture | | | Organic Layer | | | Water Layer[a] | |
|---|---|---|---|---|---|---|---|
| Wt. % aniline | Wt. % toluene | Wt. % water | Wt. % aniline | Wt. % water | $n_D^{25}$ | Wt. % aniline | $n_D^{25}$ |
| 19.41 | 3.34 | 77.25 | 78.7 | 3.3 | 1.5605 | 3.1[b] | 1.3384 |
| 15.79 | 6.70 | 77.51 | 65.1 | 1.9 | 1.5477 | 2.7[b] | 1.3378 |
| 11.93 | 10.12 | 77.95 | 50.7 | 0.7 | 1.5336 | 2.3[b] | 1.3372 |
| 7.99 | 13.57 | 78.44 | 34.0 | 0.25 | 1.5200 | 1.9[b] | 1.3359 |
| 4.03 | 17.06 | 78.91 | 15.5 | 0.07 | 1.5048 | 1.2[b] | 1.3344 |

[a] Toluene in water layer always below 0.06%.
[b] By analysis.

Because of the low solubilities it is difficult to use data as presented in a conventional ternary diagram (Figure 2). The composition of organic and aqueous layers in equilibrium may best be obtained from Figures 1 and 3, or Figure 1 and Equation 1. For example, an organic layer containing 75% aniline will contain 2.9% water, as shown in Figure 1, and 22.1% toluene. From Figure 3, an organic layer containing 75% aniline will be in equilibrium with an aqueous layer containing 2.97% aniline. Thus, assuming that the aqueous layer contains 0.05% toluene, an organic layer containing 75% aniline, 2.9% water, and 22.1% toluene will be in equilibrium with an aqueous layer containing 96.98% water, 2.97% aniline, and 0.05% toluene.

## ACKNOWLEDGEMENT

The authors wish to thank R. T. Morris, who did the analytical work.

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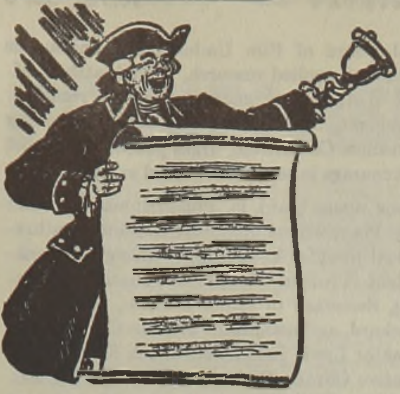

# MAY'S HEADLINES

## Events during the Month, of Interest to Chemists, Chemical Engineers, Executives

## *Reviewed by the Editors*

¶ May 1. War Production Board estimates military consumption of copper will fall 15% with shift to one-front war.∼∼Devoe & Raynolds acquires Trucson Laboratories of Detroit.∼∼Producer announces cut in penicillin price to hospitals to $1.10 per 100,000 units.∼∼President Truman cuts estimate for Office of Scientific Research and Development $13,200,000.∼∼Blaw-Knox purchases Buffalo Foundry and Machine Co.

¶ May 2. WPB revokes three orders restricting controls on printing inks, calcium metal, and nitrocellulose.∼∼House Select Committee on Postwar Military Planning recommends passage of H.R. 2946 which provides that Government appropriate funds annually to National Research Council for scientific research in interest of national security.

¶ May 3. Lederle Laboratories release "veticillin", a penicillin developed for veterinary use.∼∼WPB bars use of imported cane alcohol for blending beverage spirits and miscellaneous uses.

¶ May 4. Senate committee hearings on carbon black shortage bring Senate charges of an industry strike against production expansion and testimony that WPB compromised with the industry.∼∼Witco Chemical observes 25th anniversary[1].

¶ May 6. WPB places container board, including solid and corrugated fiber sheets, used in manufacture of fiber containers and boxes, on National Production Urgency List.∼∼H. L. Derby, president, Manufacturing Chemists' Association, in coast-to-coast radio address, says chemical industry has met wartime challenge by more than trebling output since 1939.

¶ May 7. Foreign Economic Administration says penicillin is available for export commercially to all areas.∼∼Scrapped planes yield chemically pure aluminum by process developed by research engineers of Aluminum Ore Co., working with engineers of Air Technical Service Command and Redistribution & Salvage Office of Army Air Force.∼∼WPB directs production of 46,300,000 pounds of rayon tire yarn by American Viscose to meet critical shortage, W. C. Appleton, company president, says.∼∼Chief Justice Stone names Federal Judge Charles E. Wyzanski, Jr., to try suit of Standard Oil of N. J. against Alien Property Custodian in New York May 21.∼∼H. Leroy Whitney, former technical adviser to Donald M. Nelson, tells Senate investigators shortage of carbon black is due to lack of push by top WPB officials for a program recommended a year ago.∼∼Germany surrenders unconditionally to Western Allies and Soviet Union at Reims at 2:41 A.M., French daylight saving time.

¶ May 8. House committee, created to study economic policy and planning, outlines 15 steps to increase international trade.

¶ May 9. Peace in Europe came technically at 12:16 A.M. Berlin time.∼∼WPB releases idle and excess stocks of steel, copper, and aluminum for delivery after July 1 for civilian goods.

¶ May 10. FEA says Argentina's exportable surplus oilseeds and their products will be purchased, and petroleum will be furnished in return for linseed oil diverted for use as fuel.

¶ May 11. John W. Thomas, chairman, Firestone Tire & Rubber, in medal award address before American Institute of Chemists, says science, with its limitless capacity for eliminating want and creating plenty, may develop formula for lasting peace.

¶ May 13. Secretary of Commerce Wallace issues instructions to agencies to start planning services to aid industry's changeover from war to peace.∼∼Use of glycerol in explosives to clear war-devastated areas is expected to approximate wartime use of glycerol in military ammunition, according to Bureau of Foreign and Domestic Commerce.∼∼WPB amends Conservation Order M-112 because of critical shortage of antimony and antimony oxide; purchasers are now required to certify as to their needs.

¶ May 14. Interior Secretary Ickes, speaking before Senate Subcommittee Investigating Small Business, urges that Government cut back aluminum contract with Canada and utilize domestic facilities to fullest extent and that independent enterprises be given a chance to take over government-built aluminum plants. Ickes says U. S. industry is competing with Canadian plant built with U. S. funds.∼∼WPB Chairman Krug asks government procurement agencies to cancel orders for shipment of containers not required as result of contract cancellations.∼∼Edwin R. Gilliland, former Assistant Rubber Director, in accepting Leo Hendrick Baekeland Medal, North Jersey Section, ACS, predicts that synthetic rubber will equal performance of natural rubber in all uses within 5 years.∼∼WPB lifts restrictions on manufacture of paper mill machinery and wire cloth used in production of pulp and paper.∼∼WPB says no additional steel will be allocated to can manufacturers for second quarter of 1945.∼∼WPB sets aside 240,000 pounds of hydrogen peroxide for use in May and June to prevent shutdowns in civilian goods industries.∼∼Former Rubber Director Bradley Dewey tells Senate Defense Investigating Committee that carbon black cut in synthetic rubber tires is a terrible thing.∼∼WPB amends Schedule 17 of M-300 on acrylic monomer and acrylic resin to bring them into line with amendment easing controls on sale of surplus stocks.

¶ May 15. WPB recommends drastic cut in purchases of aluminum from Aluminum Co. of Canada's Quebec plants.∼∼U. S. paper and paperboard output for first quarter of 1945 about 2% less than authorized minimum production.∼∼Defense Plant Corp. announces that three magnesium plants are being returned to full production schedules at request of WPB.∼∼Du Pont and Rohm & Haas charged in U. S. District Court, Newark, N. J., with conspiring with individuals and interests in Germany to control manufacture and sale of acrylic plastic materials.∼∼WPB Chemicals Bureau officials tell Cellulose Acetate Molding Powder and Sheeting Producers Industry Advisory Committee production

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[1] *Chem. Eng. News*, 23, 814 (May 10, 1945).

rate of cellulose acetate molding powder has been maintained at about 4,000,000 pounds per month for past 9 months.

¶ MAY 16. S. T. Crossland, executive vice president, Rubber Reserve Co., says synthetic rubber industry must produce at 124% of rated capacity in 1945 and at 145% in 1946 to meet demands of armed services, and civilian and export uses.∼∼Chicago Section, ACS, awards 1945 Willard Gibbs Medal to Frank C. Whitmore, Dean of Pennsylvania State College and an ACS past president.∼∼Metals Reserves Corp. cuts purchase contract for 250,000,000 pounds of aluminum from Aluminum Co. of Canada's Quebec plants to 150,000,000 pounds.∼∼Petroleum Administration for War predicts crude oil production this year will increase 150,000 barrels daily over recorded average of 1944. ∼∼Federal Loan Administrator says Government will continue to buy manganese and chrome ore, at least until end of year. ∼∼Assistant Attorney General Wendel Berge advises Washington Trade Association Executives of procedure to follow in postwar without trespassing on antitrust laws.

¶ MAY 17. Attorney General Biddle and Assistant Secretary of State Clayton support O'Mahoney Bill which would bar secrecy in international agreements.∼∼Westinghouse awards George Westinghouse Scholarships, each valued at $1850, to ten pupils who will attend College of Engineering at Carnegie Institute of Technology.∼∼Assistant Secretary of State Clayton announces at Senate hearing that State Department will try to outlaw cartels through international agreement.∼∼War Manpower Commissioner delegates discretionary authority to regional directors to revoke 48-hour week in 28 areas.∼∼WPB amends Schedule 71 to clarify definition of imported ethyl alcohol.

¶ MAY 18. Assistant Attorney General Berge tells joint meeting of Senate Judiciary Subcommittee and Committee Investigating Petroleum Resources our national security has often been endangered by American businessmen in their cartel policies.∼∼WPB issues list of materials which it believes will continue in short supply.∼∼WPB again permits use of naphthenate driers for army paints.

¶ MAY 19. Orville Harden, vice president, Standard Oil of N. J., in unscheduled appearance before Senate Judiciary Committee, defends prewar cartel agreements.∼∼WPB places sodium metasilicate under allocation control of Schedule 106 of Order M-300, general chemicals allocation order.∼∼WPB says superphosphate industry is willing to expand to meet requirements.

¶ MAY 21. R. J. Dearborn, president, Texaco Development Corp., and chairman, Patents Committee of National Association of Manufacturers, says postwar expansion of industrial research by small companies will be limited by scarcity of scientific and technical men.∼∼I. W. Wilson, vice president, Aluminum Co. of America, in letter to Chairman Murray cites "glaring misstatements" by Secretary of Interior Ickes before Senate Small Business Committee, "resents unfair criticism based on misstatement of fact", and asks that record be set straight.∼∼University of North Carolina discovers new sources of tannin in southeastern trees.∼∼Trial, instituted by Standard Oil of N. J. to recover 2500 patents seized by Alien Property Custodian in 1942 and 1944, begins.∼∼W. S. S. Rodgers, Chairman of Board, Texas Co., testifies at hearing of Special Committee Investigating Petroleum Resources that, unless foreign governments adopt American competitive system, domestic oil interests may be forced to abandon position in foreign markets.∼∼Justice Department wins case in U. S. Supreme Court against Alkali Export Association under antitrust laws, independently of whether Federal Trade Commission has originally questioned legality of operations.∼∼Senate confirms David E. Lilienthal as chairman of TVA for another 9-year term.∼∼Aluminum Co. of America denies Secretary of Interior Ickes charges that it has any connection with Aluminum Co. of Canada.

¶ MAY 22. National Board of Fire Underwriters announces establishment of division of applied research, with Matthew M. Braidech, Case School of Applied Science, director of research. ∼∼Emil Schram, president, N. Y. Stock Exchange, appearing before House Small Business Committee, urges postwar tax relief for small business to encourage investment of local capital.

¶ MAY 23. Blaw-Knox opens plant in Philadelphia for Solid Fuels Administration. Plant will manufacture combined anthracite and bituminous coal product known as "white glove packaged fuel".∼∼President Truman accepts resignation of Attorney General Biddle, Secretary of Labor Perkins, and Secretary of Agriculture Wickard, and nominates Thomas C. Clark Attorney General, ex-Senator Lewis L. Schwellenbach Secretary of Labor, and Representative Clinton P. Anderson of New Mexico, Secretary of Agriculture.∼∼Philip W. Amram, Special Assistant U. S. Attorney, in Federal Court accuses Standard Oil of N. J. and I. G. Farbenindustrie of pooling patents to create a worldwide partnership.∼∼Justice Department charges Libbey-Owens-Ford Glass Co., Pittsburgh Plate Glass Co., and seven other manufacturers with conspiracy to eliminate competition in flat glass industry.∼∼WPB announces appointment of reconversion chairmen for approximately 400 industries.∼∼Charles D. Robeson and James G. Baxter of Distillation Products, Inc., announce discovery and isolation of new vitamin A in fish liver oils.∼∼Pennsylvania Grade Crude Oil Association opens new phase of petroleum production research based on role of bacteria in petroleum production operations.

¶ MAY 24. WPB authorizes beverage alcohol "holiday" for month of July.∼∼President Truman asks power for unlimited changes in administrative set-up of Government to make executive branch "more businesslike and efficient".∼∼Glenn L. Haskell, president U. S. Industrial Chemicals, says on June 1 Dodge & Olcott, essential oil company, will be merged with it.∼∼Wm. P. Boyd, Jr., president American Petroleum Institute, announces organization of Medical Advisory Committee to promote additional studies in arts and sciences connected with petroleum industry.∼∼Wm. J. Robbins, director N. Y. Botanical Garden, announces discovery of six new antibiotic substances that resemble penicillin in inhibiting growth of other microorganisms.∼∼WPB and Surplus Property Board combine with separate actions to accelerate reconversion.∼∼Secretary of Commerce Wallace urges U. S. to lower tariffs and trade with other countries on a live and let-live basis.

¶ MAY 26. House of Representatives votes tariff bill to extend and broaden reciprocal trade program.∼∼American Museum initiates 3-year preliminary survey of biogeochemistry.

¶ MAY 27. WPB Chairman Krug assures industry all possible regulations and production restrictions will be lifted after Japan's defeat.

¶ MAY 29. Eastman Kodak officials reveal plans for two large buildings to be erected as soon as possible after the war at a cost of "several million dollars".∼∼Government begins suit to settle old question as to who owns oil deposits under coastal waters of U. S.∼∼Lt. Gen. Wm. S. Knudsen, director of production, will retire June 1, War Department announces.

¶ MAY 30. WPB removes limitations on use of carbon black in tires, tubes, and other rubber products, effective June 15.∼∼Department of Agriculture's northern research laboratory, Peoria, Ill., makes liquid motor fuel from corn cobs, oat hulls, peanut shells, and other waste farm materials, J. M. Dunning, one of scientists developing process, says.

¶ May 31. General Electric President Charles E. Wilson says company will build $8,000,000 research laboratory in Niskayuna on Mohawk River cliff.∼∼Senate confirms Lewis B. Schwellenbach as Secretary of Labor.∼∼WPB amends order M-387 for rosin to make it more workable for industry.

# Current Developments in EQUIPMENT AND DESIGN

*"The skill, not the quickness, of the hand and the eye..."*

### Discussed by Charles Owen Brown

MUSING over the changes in industry which V-E day must surely bring, a picture comes to mind of the great manufacturing accomplishments of the war era. Gas compressors, ship turbines, and airplane engines, totaling millions of horsepower, have not always been made by one skilled experienced group of craftsmen under a unified control and individual over-all supervision; yet these machines have not only worked but have been marvels of efficiency. Perhaps you do not know how thirty-eight separate scattered subcontractors have supplied component parts of airplane engines or ship turbines. The answer was supplied recently by President Harrington, of the Savage Tool Company. He described the exacting measurement of the dimensions of these parts by the methods and with the tools to be reported here. The familiar fractions, such as $^{23}/_{32}$ inch, which once appeared between the arrowheads on shop blueprints have largely disappeared. We are now likely to see 0.71875 + 0.00005 − 0.0001 inch, or some such tolerance variation. This new style of expression has much to do with the success of recent mechanical marvels, because the common fractions $x/16$, $x/32$, and $x/64$ inch were too rough to express dimensions of the order of one half of one ten-thousandth of an inch as given above. More amazing yet is the knowledge that the tools used at the machine and workbench to detect 0.0001 inch are inspected and tested for wear by master gages accurate to one or two millionths of an inch. While all chemists and physicists are reasonably familiar with Michelson's interferometer, they may not know that gages by the hundreds are used daily which are proved accurate to less than 0.000001 inch by simple applications of the interferometer principle.

What does a dimension of the size of 0.000001 or a micro inch mean? An experienced, steady hand, using a high quality C-shaped micrometer caliper, can feel dimensional variations of 0.001 inch; and with a friction-head to give a constant setting pressure, 0.0002 inch can be "felt", but not accurately. The eye is not much better, either in plain reading or in guiding the hand. A steel rule can be read to $^1/_{64}$ inch by normal vision in good light, sometimes to 0.01 inch. Trammel points can be set by a steady workman, who has "lived right", to approximately 0.003 inch. The eye can detect white light through a slot 0.0001 inch wide, largely because of the help of the light. But these dimensions are a long way from 0.000001 inch.

The use of a light beam is the key to fine measurement. To visualize the matter more easily, let us assign a value to the thickness of a silver 10-cent piece as 0.000001 inch. Then one full inch would consist of a pile of dimes stacked face to face, over 0.850 mile high. Each dime in that pile has the same relative magnitude as 0.000001 inch to a full inch. To detect the loss of several dimes from the top of that pile would be impossible by direct vision. With the aid of suitable light waves, the matter becomes simple, but it is not easy to explain this technique within the space of this column. Therefore, this subject will be continued in the July "Equipment and Design" pages.

Let us start with three pieces of fused quartz, because of its low coefficient of thermal expansion, clear bright optical transparency, and hardness. Each piece is shaped into a disk 4 or 5 inches in diameter and about 1.0 inch thick, by machine grinding; then each is lapped and polished until

(*Continued on page 76*)

INTERFERENCE OF HELIUM LIGHT WAVES

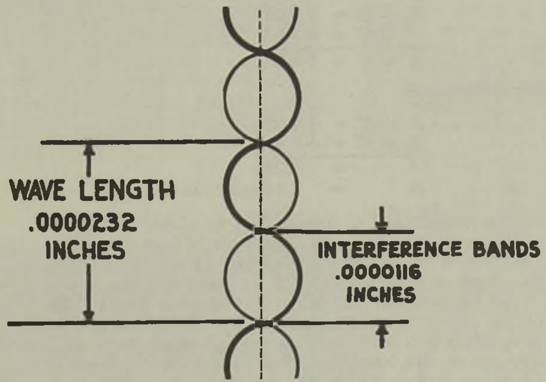
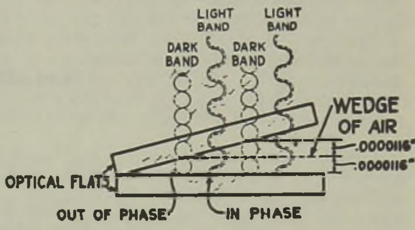


Figure 1

APPLICATION OF HELIUM LIGHT WAVES TO MEASUREMENT



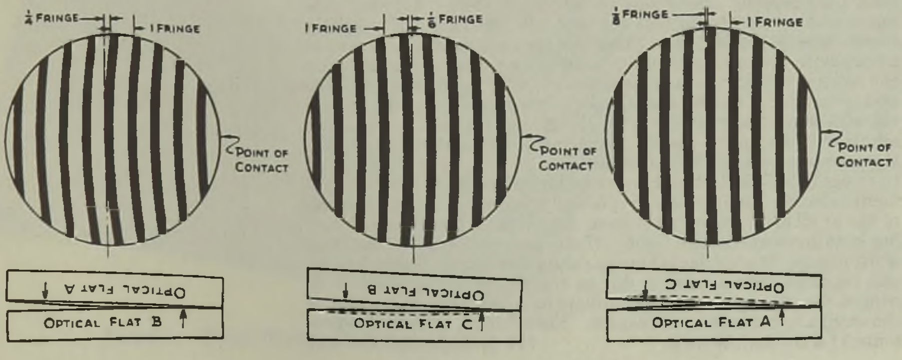


Figure 2

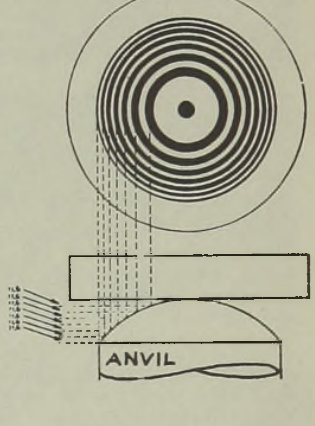


Figure 3

it has a brilliant surface, apparently flat with both sides parallel. These tools are known as optical flats. The next problem is to inspect their surfaces and prove that all variations from true level or flatness are of the order of 0.05 wave length, or 0.000001 inch. A dependable source of light must be used to produce a definite wave length, and industry has selected the yellow of helium because this gas can be purified to a high degree. Its wave length is 5750 to 6005 Å., or 22.6 to 23.6 micro inches, with an average value of 23.2 micro inches. The development of interference bands in light waves of helium by a wedge of air between two optical flats is represented simply in Figure 1. When the light wave passing through the upper flat is reflected from the lower flat surface completely out of phase with a second wave, the amplitudes neutralize each other; a dark band then appears, roughly represented by the first and third waves from the left. When two waves pass through the air gap where the depth of air is correct to put them in phase, no dark fringe appears, and in this manner the top view of an optical flat under monochromatic light is a series of spaced dark bands. The pattern and curvature of these bands are read like a contour map to interpret the hills and valleys in the surface between the optical flats.

To determine how true and parallel the surfaces have been made by the lapping operation, these flats will be designated as *A*, *B*, and *C*. First we put flat *A* on flat *B*. The left-hand diagram of Figure 2 shows the black band curving with the center to the left. The amount of this curvature is approximately one quarter of a fringe. One fringe is the distance between the corresponding edge of two black bands. Since monochromatic light has a wave length of 0.0000232 inch, and since the black and white bands are one half wave length, each band represents 0.0000116 inch. Therefore, *A* on *B* represented by the left-hand diagram is:

$$+\tfrac{1}{4}\text{ fringe or }\tfrac{1}{4}\text{ of }11.6 = +2.90\text{ micro in.} \qquad (1)$$

*B* on *C* curving the opposite way is:

$$-\tfrac{1}{6}\text{ fringe} = -\tfrac{1}{6}\text{ of }11.6 = -1.93\text{ micro in.} \qquad (2)$$

$$A\text{ on }C = +\tfrac{1}{8}\text{ fringe} = \tfrac{1}{8} \times 11.6 = 1.45\text{ micro in.} \qquad (3)$$

These equations are solved by subtracting 2 from 1,

$$\begin{array}{rcl} A + B &=& +2.90 \\ B + C &=& -1.93 \\ \hline A - C &=& +4.83 \end{array}$$

and adding Equation 3,

$$\begin{array}{rcl} A - C &=& +4.83 \\ A + C &=& +1.45 \\ \hline 2A &=& 6.28 \\ A &=& 3.14\text{ micro in.} \end{array}$$

Now *A* can be substituted in Equation 1 to obtain: $3.14 + B = +2.9$; $B = -0.24$ micro inch. Similarly, *C* is obtained by: $0.24 + C = -1.93$; $C = -1.69$ micro inches. From these equations and the values of *A*, *B*, and *C*, it is a simple deduction that optical flat *A* is 3.14 micro inches high in the center, shown by the regularity of the arc of the dark bands. Optical flat *B* is 0.24 micro inch low, fairly well confined to the center of the flat owing to the regular arc of the bands curving to the right. Optical flat *C* is 1.69 micro inches low in the center. From this data, skillful operators of the DoAll Company, of Des Plaines, Ill., and Savage, Minn., will be able to correct the imperfection by continued lapping operations on the high spots. Optical flats made and calibrated in this manner are essential for the daily measurements on tools and other instruments to determine their accuracy in much smaller units than the dimensions required on the work on which the instruments are used. For example, the end or anvil of a micrometer caliper screwstem first grows spherical with wear, and next the actual length of the anvil decreases in addition to becoming round. It is therefore essential to inspect the micrometer anvil to determine just how badly it is worn and to reject it before it causes errors or faulty work. This measurement is rather easily made by placing the optical flat on the end of the anvil after removing it from the *C* frame and then subjecting it to monochromatic light. If the end of the anvil has been worn in a fairly spherical shape, as shown in Figure 3, the fringes will be concentric around a dot in the center. The number of fringes determine how many millionths of an inch the edges of the anvil are lower than the center. Each fringe, as before, represents 11.6 millionths inch.

*(To be continued in July)*

# *Current Developments in*
# INSTRUMENTATION

What about competition in the international instrument field in postwar?

### *Discussed by Ralph H. Munch*

An article by Reginald S. Clay, entitled "Suggestions for the Reorganization of the Instrument Industry after the War", appeared in the March *Journal of Scientific Instruments.* He is concerned primarily with the British instrument industry, but all users and makers of instruments should be interested in the ideas expressed. Clay foresees keen competition for the British from France, Italy, Switzerland, Czechoslovakia, the United States, and probably Russia. He most fears competition from the United States because our instrument industry has been less disorganized by the war than the British, and because we have been able to maintain exports and capture foreign markets even in British dominions during the war period. He also fears small-scale competition with our mass production methods, and competition by small firms without adequate research staffs with larger firms maintaining staffs of technically trained research men. He has heard a report that major instrument makers here have organized themselves so that each specializes in the manufacture of a given instrument and does not compete with the specialty of other firms in the organization.

Clay explores three means to enable the British instrument industry to compete. He believes that the first, protective tariff, could be maintained only as long as the government considers the instrument industry deserving of protection, and that it would not enable them to compete in foreign markets. The second is an organization of instrument makers to restrict competition and duplication of effort. He considers this idea in some detail, starting with a simple agreement among manufacturers to specialize in a given instrument and not to compete with the specialties of others, and progressing to complete amalgamation of all firms making a given type of instrument into a single noncompeting unit; the resulting firms would become the British Electrical Instrument Company, British Microscope Company, and so on. This second means, he thinks, could be worked out but might suffer later from competition with nations having unlimited supplies of cheap labor. His third possibility is for the British instrument makers to concentrate on the manufacture of new and more specialized apparatus for which small-scale production methods would be most suitable and for which the market is largely independent of labor costs. To be successful in this line of endeavor, he believes that scientific research would be a prime requisite; joint research staffs maintained by the instrument manufacturers and the pooling of knowledge and experience would give maximum efficiency. Government subsidy of research for instrument development is mentioned. Finally, to sell the products of this highly developed specialty instrument group, Clay proposes a world-wide sales organization.

We in the United States should be interested in these proposals. Our larger manufacturers produce instruments second to none, but some of them have a tendency to make only those items for which the market is large. There is, however, a real need for various types of highly specialized instruments where the quantities involved are not attractive to large firms. Before the war European firms filled our requirements for these specialties. During the war several small firms have gone into the field. It is to be hoped that these and others like them will develop into a group capable of supplying our laboratories with specialized instruments. Permitting others to fill our needs is not conducive to rapid scientific advance in this country.

## *Flame Photometer*

Quantitative analyses for sodium and potassium have long been among the troublesome and unsatisfactory analytical procedures. Chemical methods are slow, some require expensive reagents, all need careful manipulation. Spectrographic methods are more rapid, but require expensive equipment and trained personnel. To improve this situation, the Perkin-Elmer Corporation (Glenbrook, Conn.) has placed on the market an instrument known as the Model 18 flame photometer. This instrument measures the intensity of sodium or potassium radiation emitted when an aqueous solution of the unknown is atomized into a flame

Figure 1. Flame Photometer (Perkin-Elmer)

The essential parts of the flame photometer (Figure 1) are a special Mekker burner, an atomizer to convert the sample solution to mist and introduce it into the burner flame, a lens system to concentrate light from the flame onto the cathodes of two photocells, filters to minimize the effect of light emitted by other elements, and a thermionic amplifier and meter to measure the photocell currents. One photocell filter combination is sensitive to sodium radiation and the other to potassium radiation. The amplifier has two sets of zero and sensitivity controls; one is for sodium, the other for potassium, so that the calibrations need not be disturbed when switching from one analysis to the other.

Calibrations are obtained by running several known solutions. The instrument may be set to have full scale equal any desired concentration of sodium or potassium from 15 to 1000 p.p.m. One tenth part per million can be detected. In routine operation the makers state that the accuracy is ±3% of the amount present with a single reading, and that an accuracy of ±1% is possible by averaging ten readings. A single reading requires about 10 cc. of sample and can be obtained in 2 minutes. The effect of foreign ions is not appreciable unless they are several times as concentrated as the sodium or potassium. Relatively untrained personnel can operate the instrument with ease and accuracy.

The flame photometer should find wide use wherever analyses for sodium or potassium are needed, especially where previous methods could not be justified because of slowness or expense. Such applications should include soil analyses, water analyses, clinical analyses, catalytic studies, and many others.

(*Continued on page 82*)

## Electrical Pressure Transmitters

The Statham Laboratories (Los Angeles, Calif.) are now producing remote-indicating pressure transmitters. The sensitive element is a bellows for pressures below 20 pounds per square inch or a diaphragm for pressures above that value. Motion of the bellows or diaphragm is detected by an unbonded strain gage. Strain-sensitive filaments mounted in grid form make up the four arms of a Wheatstone bridge. The bridge is permanently connected and balanced inside the instrument. This type of construction gives good temperature stability. With a 10-volt d.c. power supply, full-scale output of the pressure transmitter can be indicated by a 150-microampere meter or recorded with conventional recording potentiometers. Normal pressure ranges are from −0.5, 0, +0.5 to −15, 0, +15 pounds per square inch. Other ranges may be obtained on special order. The instrument measures 1.25 × 1.25 × 2.5 inches and weighs about 3 ounces.

## High-Purity Gas Analyzer

The Hays Corporation (Michigan City, Ind.), manufacturer of gas analysis and combustion control equipment, has announced the development of a new Orsat type gas analyzer. Known as the Hays Series E, this analyzer was designed to fill the demand for equipment to analyze highly purified gases such as oxygen for high-altitude flying, high-purity carbon dioxide, or nitrogen.

Figure 2 shows a two-unit Series E analyzer. The left-hand unit is for the analysis of gases such as oxygen or carbon dioxide where the major constituent is absorbed; the right-hand unit is for the analysis of gases such as nitrogen where the impurities are absorbed. Single-unit models are also available. These analyzers feature metal construction with a minimum of glass parts. The usual glass stopcock has been replaced by a four-way metal valve which controls sample flow. This construction should help eliminate sticking stopcocks and breakage of glass parts. The plastic shield should also help avoid breakage of glass parts.

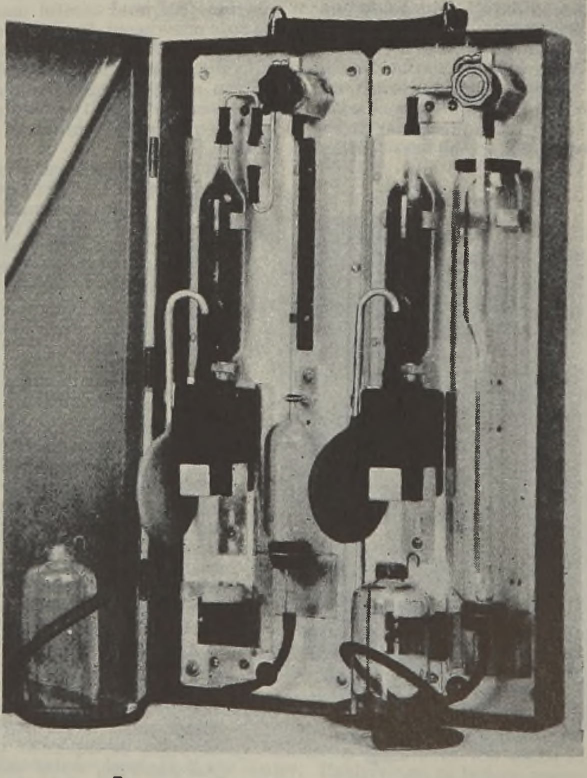


Figure 2. Gas Analyzer, Hays Series E

# Current Developments in PLANT MANAGEMENT

Means of reducing waste caused by employee carelessness are discussed.

### Discussed by Walter von Pechmann

Supervisors frequently state that spoilage in production caused by the negligence of workers cannot be avoided, since management nowadays hesitates to discipline careless workers. This point of view, if shared by management, results in foremen taking excessive spoilage as an unavoidable adjunct of present-day conditions. Furthermore, management's admission that it is not in a position to cope with this situation is considered by supervisory personnel as weakness. Loss of prestige on the part of management and loss of interest in work by foremen are generally the aftermath of this condition.

The usual remedy suggested to reduce spoilage due to carelessness is fostering employees' interest in their work either by appealing to patriotism or offering rewards for reduced spoilage. Morale builders are usually effective; however, workers must be convinced that management is mainly interested in the reduction of spoilage for the sake of the Nation and not because of increased revenues. Opinions vary considerably as to the merit of paying workers for reduced spoilage. Some believe that this method is effective; others claim that the compensation for excessive waste reduction will not decrease spoilage since workers who do not take advantage of the bonus and, therefore, retain a high record of waste, cannot be reprimanded. Workers may claim that bonuses are paid for work performed above normal standards and, therefore, will be in a position to have management admit that it considers the prevailing material loss to be normal. My experience has been that the foreman's personal and genuine interest in the individual worker's problem is still the best way to foster employee interest in work. I prefer to invest money in a qualified industrial-relations man rather than to spend money on mass appeals or bonus payments for reduced spoilage. He can guide foremen in establishing a personal relationship between management and workers, that can be achieved only with considerable difficulty by other means in large industrial organizations.

One way often overlooked to lessen the material loss caused by carelessness is to make arrangements for reducing the alertness necessary to perform a job satisfactorily. This can be accomplished by revising and elaborating upon operating standards in such a manner that errors made by operators will automatically be called to their attention. The following examples are intended to illustrate this point and to promote interest in revising job performances so that material loss can be reduced, even though workers' carelessness has to be accepted more or less as a fact.

A constant source of trouble in the chemical industry seems to be spoilage due to wrong measurements and incorrect placing of ingredients prior to batch mixing. Confronted with this problem, I once decided to spend some thought and company money in making the measuring and arranging of chemicals prior to mixing "foolproof". We first coded our chemicals in such a manner that those belonging to distinctive groups of formulas were given names which are usually associated with one certain thought. Some ingredients, for instance, were given the names of flowers; others were given the names of cities. Even a careless worker would now notice if he had put together ingredients which did not belong to the same group of formulas. The identical separation made by code numbers and letters had not been effective or prevented mix-ups.

The next step was what we called the "destandardization" of containers. The practice was abolished of using identical vessels to indicate the chemicals contained. Instead, the vessels were selected so that they were always at least half filled when the ingredients were properly weighed or measured. The chemical identification was changed to a symbol such as square, round, or oval dots painted on boxes and bottles. Colored bands and strips

(*Continued on page 88*)

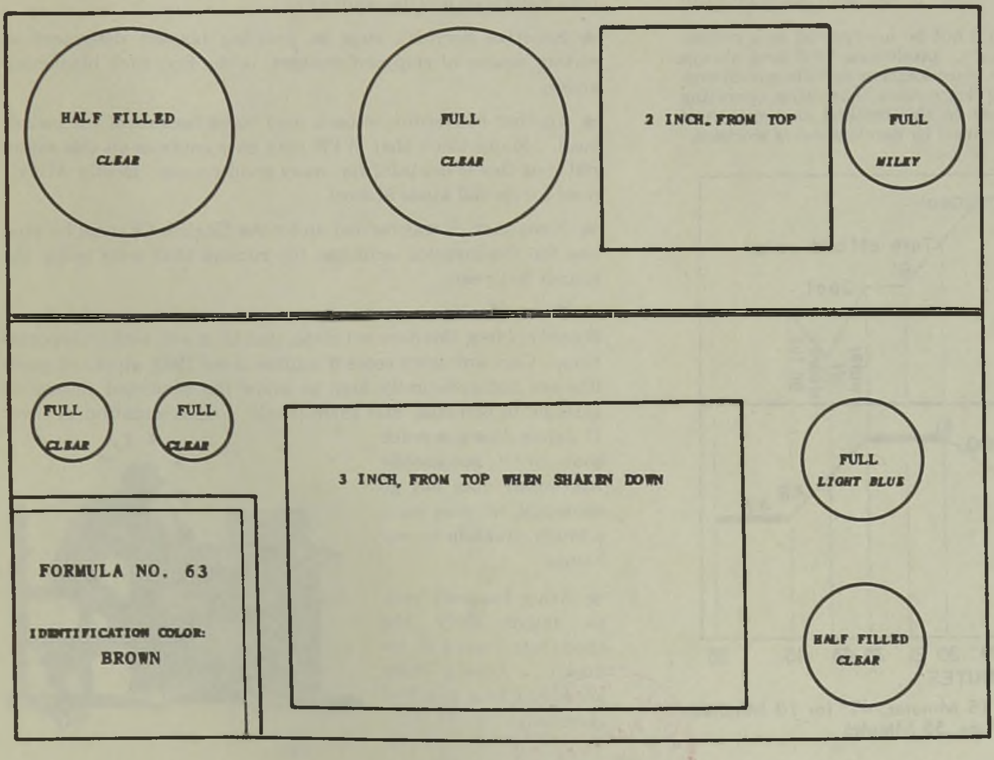


Figure 1. A Typical Template Designed to Prevent Errors of Operators in Assembling Chemicals for Specific Formulations

were used to indicate specific formulas, and the storage of the premarked containers was arranged close to the bins and tanks holding the bulk material. When preparing a batch, operators now simply select containers by symbol and color. Should a container belonging to one formula accidentally be mixed with a container belonging to another, this error will be noticed without difficulty by operators since the colors will not match, and two identical symbols will be contained in one batch prepared.

As a further safeguard, templates were made for each formula, as Figure 1 shows. The operator preparing the formula has to place each container on the template. If he forgets to measure an ingredient, his attention will be called to his negligence by the empty space on the template. The description on the template, which states how far the containers have to be filled to comply with requirements, makes it also possible to detect errors made in weighing and measuring. We gradually elaborated upon this system by making the templates of wood and using them as trays which could be placed on trucks. We painted on the templates the job performance instructions such as temperatures, time cycles, mixing speed, etc. This again reduces the possibility that workers in the mixing room will receive the chemicals for one formula and use job performance instructions for another.

Another simple method also reduces waste. Operators are supplied with a measuring stick on which are marked the number of containers used as well as the heights of ingredients inside each container. Before delivery of the chemicals into the workrooms, operators are requested to place the stick alongside each container to determine if the measurements or weights are approximately correct. They also are instructed to count the number of containers and to compare their findings with the writing on the stick. This method is not so effective as the one previously described because supervision has to depend on the worker's measuring each container, whereas the method where templates are used automatically calls attention to errors.

Figure 2 is designed to tell operators when and how to operate a kettle to expose a product to various temperatures during one process. The graph marked "outside" gives operating instructions as well as temperatures prevailing in the water jacket at various stages of the process. The graph marked "inside" gives the temperatures of the product in the container if instructions are properly followed. Not only have I found this medium of instruction helpful in preventing overheating due to lack of alertness on the part of workers, but also have been able to train employees in the operation of kettles in less than one quarter of the time usually required.

The methods described should not be interpreted as a recommendation for general acceptance; production problems always have to be solved, taking into consideration specific conditions. It is hoped, however, that this description of revising operating standards will stimulate interest in this method as a means of eliminating or lessening waste caused by carelessness of workers.

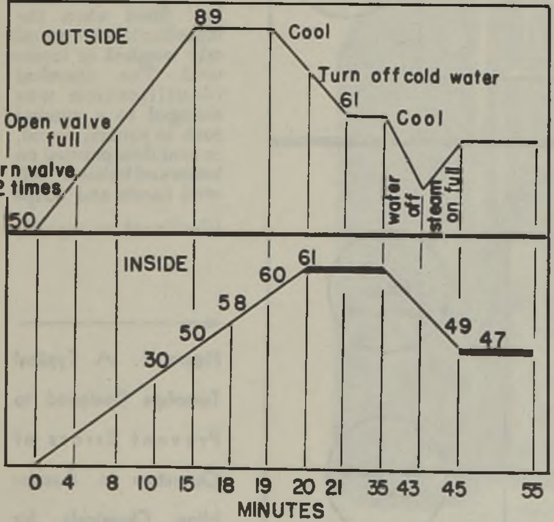


**Figure 2.** Formula 64: 61° for 15 Minutes, 47° for 10 Minutes, Total Heating Time, 55 Minutes

# *Last-*[illegible]

# FROM THE EDITOR'S DESK

In the past eleven months the Office of Surplus Property has sold 131 million dollars worth of consumer goods. For the month of April they sold, for almost 5 million dollars, material which cost about 14 million when new.

★ Washington is predicting shipments of wood pulp from Sweden very shortly.

★ A new bill is reported pending in Congress which will place an additional levy on pay rolls. It is in conjunction with social security legislation and is designed to pay for health insurance.

★ Sulfur sales reached an all-time high during the first quarter of this year. Totals were approximately a million tons. Previous record for a comparable period was in 1944 when 800 thousand tons were sold.

★ The British Ministry of Agriculture, experimenting with hexachlorobenzene, announces it is a better insecticide for ticks and mites than DDT.

★ Australia has almost doubled importation of fertilizers during the last year, and has passed her prewar record.

★ According to underground reports from the Dutch East Indies, the Japs have not destroyed the cinchona trees but have been producing quinine at a substantial rate for their own nationals.

★ A strange shortage may limit conversion to civilian goods, according to War Production Board. The shortage is paint, said to be due to a lack of essential chemicals.

★ Nine glass manufacturers have been named as defendants in an antitrust action brought by the Department of Justice. Named along with the companies are sixteen of their officials.

★ The cashew nut crop in India has reached a high. This means more oil for plastics makers.

★ Cotton is expected to get tighter and tighter this year as European mills open and demands grow.

★ Selective Service's step, in granting blanket deferment to certain classes of shipyard workers, is the first such blanketing action.

★ Another conversion setback may come because of the lack of steel. Many think that WPB may ease controls on this material, but this is doubtful for many good reasons, mostly Army's need for special kinds of steel.

★ News that oil was carried under the English Channel by pipe line for the invasion confirms the rumors that were going the rounds last year.

★ Although there is now an increase in gas allotments for A and B card holders, this does not mean that all is well with transportation. Cars are down some 4 million since 1942, stocks of gasoline are not sufficiently high to allow the predicted release of gasoline to civilians, and there is still a tight situation in tires If Japan does not crack soon or if automobile conversion does not go smoothly, we may have a tough situation on our hands.

★ Army has sent back to active duty the specialists loaned to industry. Among them are about four hundred chemists.